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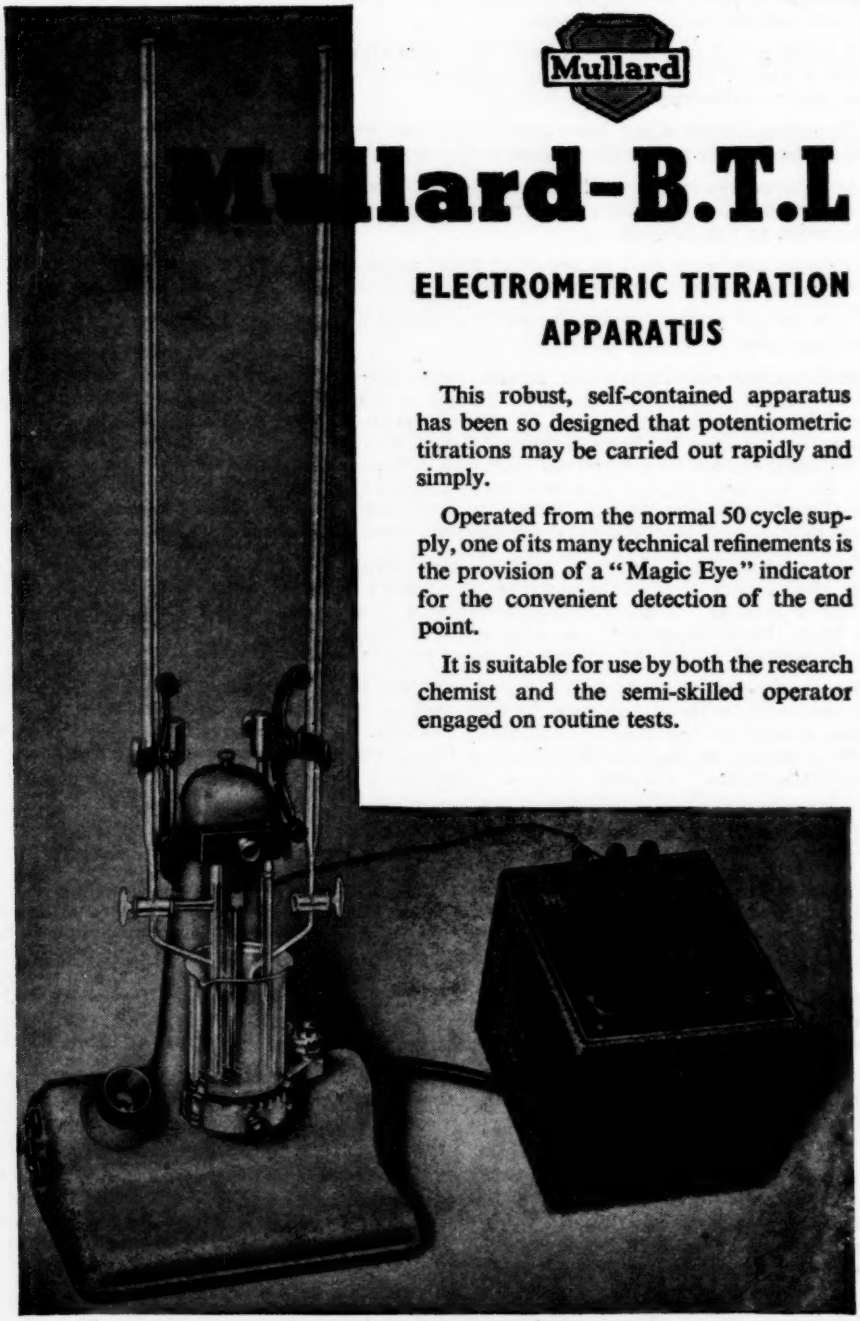

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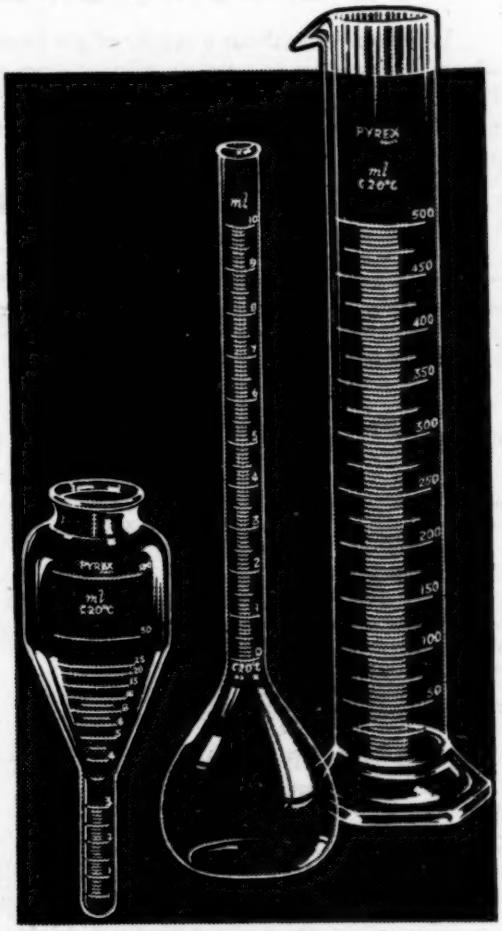

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Prideaux wrote several books: "The Theory and use of Indicators," "Problems in Physical Chemistry," and "A Survey of English Elementary Education." He was the author of the volume "Phosphorus" in Newton Friend's Text Book of Inorganic Chemistry, and joint author, with Herbert Lambourne, of the volume "Nitrogen," and with F. C. Laxton of "A Laboratory Course in Elementary Chemistry." He was, moreover, one of the pioneers in popular broadcast talks on scientific topics.

In 1908 Prideaux married the elder daughter of Rowland Bramwell, Esq., of Auckland, New Zealand. In 1946 he resigned his post as Reader in Physical and Inorganic Chemistry in the University College of Nottingham and, in recognition of his services, was awarded the title of *Lector Emeritus*. He then settled, with his wife and daughter, in his home at Canford Cliffs, Bournemouth, hoping to carry on his researches unhampered by the academic duties to which so much of his life had been devoted. The repose he had so richly earned by a life of labour was, however, denied him; he died on the 8th of May, 1946. His memory lives in the hearts of the students and friends who knew and valued him.

B. D. Shaw.

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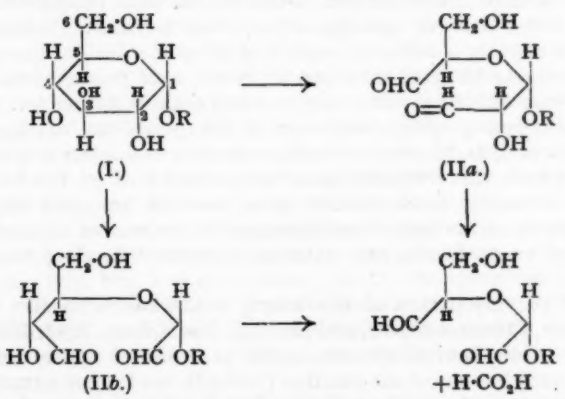
269. *Oxidation of Carbohydrates by the Periodate Ion.*

By T. G. Halsall, E. L. Hirst, and J. K. N. Jones.

The oxidation, with salts of periodic acid, of the methylglycosides of the hexose and pentose sugars and of the disaccharides has been investigated. Sugar derivatives containing hydroxyl groups on each of three adjacent carbon atoms are oxidised with the formation of 1 mol. of formic acid, and conditions have been established for the quantitative estimation of the formic acid. Methyl hexo- and pento-pyranosides and the methyl glycosides of maltose and cellobiose give rise quantitatively to 1 mol. of formic acid, but reducing sugars, methylglycosides of the uronic acids, and methylhexofuranosides yield acidic material equivalent to more than 1 mol. of formic acid per mol. of sugar. The causes of this continued oxidation are discussed.

The observation by Hudson and Jackson (*J. Amer. Chem. Soc.*, 1936, **58**, 378; 1937, **59**, 994), that the α- and β-methylglucosides yield on oxidation with periodic acid a dialdehyde together with 1 mol. of formic acid, affords a possible method of estimating the number of end groups present in a polysaccharide which has terminal groups of the type (I), provided that the non-terminal groups are such that they do not yield formic acid. Such a method should therefore be applicable to a wide range of polysaccharides, including starch, cellulose, and glycogen, which possess chains of 1 : 4-linked hexopyranose residues, but hitherto attempts to make use of this procedure have encountered difficulty in that the oxidation is not arrested at



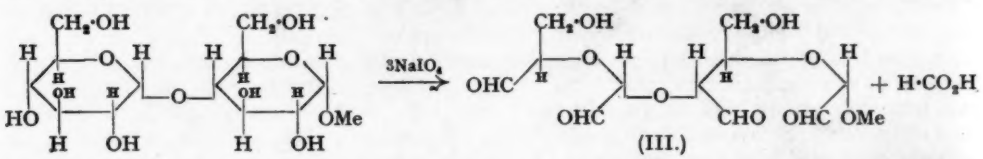
the stage when 1 mol. of formic acid has been libertated from the terminal group (Davidson, *J. Textile Inst.*, 1941, **32**, T, 109). Nevertheless the reaction has been used successfully in other

ways in the study of polysaccharides. For example, the stepwise degradation of laminarin, which consists of 1 : 3-linked residues, has been described by Barry (*Nature*, **1943**, **152**, 538) and by Dillon (*ibid.*, **1945**, **155**, 546), and attempts have been made to estimate the formaldehyde produced from the reducing end of the chain in starch dextrins (Caldwell and Hixon, *J. Biol. Chem.*, **1938**, **123**, 595).

In view of our interest in methods for estimating end groups in polysaccharides we decided to undertake a more detailed survey of the conditions requisite for the prevention of over-oxidation and thus facilitate the development of a method of estimation which would possess many advantages over the present available techniques. This was all the more necessary in that we had found in the course of experiments on plant gums, in which we had hoped to remove certain side chains with the aid of periodic acid, that difficulties due to over oxidation were encountered.

As a preliminary, therefore, to the application of the periodate method of oxidation to the polysaccharides, model experiments were carried out with simple sugars containing groups similar to those present in polysaccharides. These included α-methylglucopyranoside, α-methylgalactopyranoside, α-methylmannopyranoside, α-methyl-*d*-mannofuranoside, β-methylmaltoside, β-methylcellobioside, β-methyl-*l*-arabopyranoside, α-methyl-*d*-xylopyranoside, amygdalin, mannitol, lactose, lactal, and the methyl ester of α-methyl-*d*-galacturonoside. Control experiments with formic acid, ethylene glycol, and oxalic acid were also carried out.

It was our aim to estimate small amounts of formic acid, and this we found practicable only when the excess of periodate had been destroyed by the addition of ethylene glycol with the resultant formation of formaldehyde and sodium iodate, both of which were without action on methyl-red used as indicator for the titration of the formic acid. Sodium periodate slowly destroys formic acid, and the estimated amount of the latter may be low unless precautions are taken. It was found, however, that the oxidation of formic acid is considerably slowed down in the presence of sodium iodate, and, as this substance is always formed by reduction of the periodate, loss of formic acid during the period of oxidation is negligible. Sodium periodate gives satisfactory results for the oxidation of small amounts of methylhexopyranosides and pentopyranosides, all of which on oxidation give 1 mol. of formic acid. On the other hand when this reagent is applied to the methylglycosides of the reducing disaccharides oxidation proceeds beyond the stage represented by (III), and ultimately considerably more than 1 mol. of formic acid is produced per mol. of methylglycoside. The rate of production of formic acid is much slower, however, after the liberation of 1 mol., but with a large excess of sodium periodate as oxidising agent there is not an easy differentiation between the two stages of the reaction.

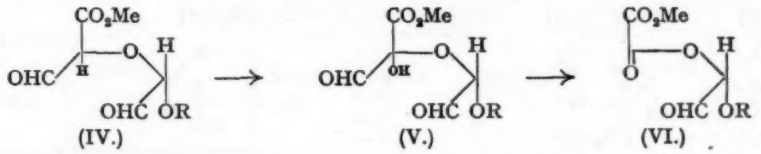


(III.)

We therefore examined other salts of periodic acid which had lower solubility and would provide reaction solutions of lower acidity. Most of the salts examined were unsatisfactory since they possessed either basic or strongly acidic characteristics. Potassium metaperiodate, however, is only very slightly soluble in water and gives a solution having a pH of about 4. Using this salt and keeping the concentration of formic acid produced to a low value (*ca.* 10 mg. per 100 c.c.), we were able to obtain consistent and reliable figures for the amount of formic acid produced. This lowering of concentration of the periodate ion, however, considerably reduces the rate of reaction, and instead of being complete in 6 hours it now requires 150 hours at 15°. On oxidation with this reagent the methylglycosides of (*a*) the hexose, (*b*) the pentose sugars, and (*c*) the reducing disaccharides gave normal amounts of formic acid. The methylglycosides of uronic acids and of hexofuranosides underwent further oxidation with the formation of additional amounts of acidic material. Similar behaviour was shown by reducing sugars.

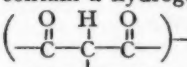
The oxidation of the glycosides of the uronic acids has been the subject of previous publications. Huebner, Lohmar, Moore, and Link (*J. Biol. Chem.*, **1945**, **159**, 502) demonstrated that, in the oxidation of zinc borneol glucuronoside, more than 1 mol of acid was produced per mol. of glucuronoside and that one of the reaction products was bornyl formate. They suggested that the uronic acid residue, after undergoing oxidation with the formation of formic acid and the dialdehyde (IV), was further oxidised by the periodate. The first step in this oxidation, it was suggested, was the oxidation of the active hydrogen situated on the carbon atom between

two carbonyl groups to a hydroxyl group (V). This would result in the formation of a substance which in its hydrated form contains hydroxyl groups on adjacent carbon atoms and would

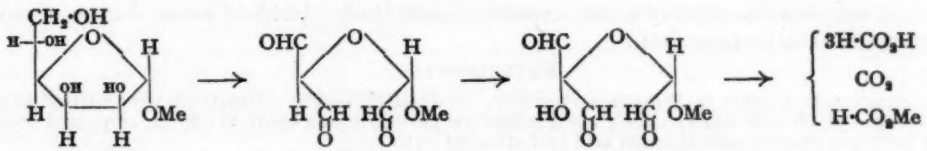


(IV.) (V.) (VI.)

undergo further oxidation with periodate with the formation of an ester of oxalic acid (VI). Once this stage had been reached the ester, which would be unstable in water, could hydrolyse to oxalic acid and a product which could then undergo further oxidation to formic acid and an ester of formic acid.

The stage in which the aldehyde (IV) is converted into the α-hydroxy-aldehyde (V) has been investigated by Sprinson and Chargaff (*J. Biol. Chem.*, 1946, **164**, 443). These workers demonstrated that substances such as malonic acid and its derivatives—substances which contain a hydrogen atom combined to a carbon atom situated between two carbonyl groups  —are all capable of being oxidised to the corresponding hydroxy-compound which may then undergo further oxidation [cf. the work of Neuberger (*J.*, 1941, 47) on the oxidation of ethyl *N*-benzoylglucosamate].

We have found that whenever this secondary type of oxidation occurs free iodine is ultimately produced and the amount of acid in the solution falls. The mode of origin of the iodine is obscure, but the simplest explanation would be to ascribe its formation to the well-known reaction between sodium iodide and sodium iodate in acid solution, the sodium iodide arising in turn from reduction of sodium iodate during oxidation on the activated carbon atom. A typical example of the grouping which undergoes further oxidation, with liberation of free iodine, is shown in (VIII) which is the intermediate product obtained by the periodate oxidation of α-methylmannofuranoside (VII). Attack at the activated hydrogen would yield (IX) which would readily undergo further oxidation giving 3 mols. of formic acid, 1 mol. of methyl formate, and 1 mol. of carbon dioxide.

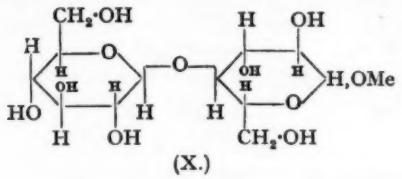


(VII.) (VIII.) (IX.)

The rate of oxidation and rate of formation of formic acid varies with the configuration of the glycoside. Those glycosides, such as the arabo-, galacto-, and manno-pyranosides, which contain *cis*-hydroxyl groups, are oxidised relatively quickly, whilst those glycosides which contain *trans*-hydroxyl groupings, such as the glucopyranosides, are oxidised more slowly (cf. " Organic Reactions ", Vol. 2, p. 353, Wiley, New York). The presence of *cis*-hydroxyl groups, however, is not the only factor which decides the rate of formation of formic acid. This is dependent also upon the rate of oxidation of the α-hydroxy-aldehyde, which is a comparatively slow reaction. Furthermore, the methylglycosides of maltose and cellobiose, both of which contain glucopyranose residues only, give formic acid at different rates. For example, methylmaltoside yields 1 mol. of formic acid in about 100 hours, whilst the cellobioside gives only 0·86 mol. in this time and 300 hours are necessary for the liberation of one equivalent of acid. This low yield of formic acid from methylcellobioside (X) could be explained by the intermediate formation of a lactol grouping such as (XI) which on further oxidation would yield not free formic acid but a formyl ester (XII). An examination of the model of the methylcellobioside molecule (and similarly of the sucrose molecule) reveals that the hydroxyl groups are so situated in space that lactol formation can readily take place, whereas the configuration of the groups in the molecule of the methylmaltoside is unfavourable for the formation of lactol groupings.

This oxidation of an intermediate lactol with formation of an ester of formic acid instead of free formic acid receives support from a study of the oxidation of mannitol. The oxidation of this hexahydroxy-alcohol yields two mols. of formaldehyde and formic acid. A quantitative

estimation of the formic acid, however, showed that the yield of this acid reached 95% of 4 mols. under the standard conditions and was not complete until the reaction had proceeded for about



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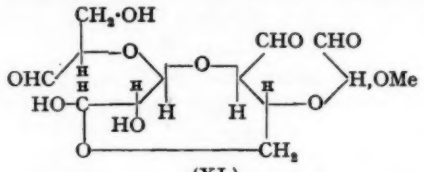

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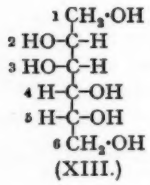

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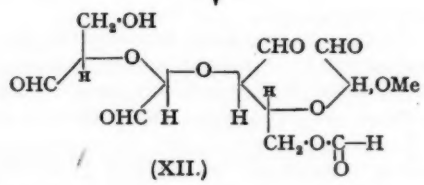

(XII.)

400 hours. The primary oxidation of mannitol (XIII) may occur in one of five places in the molecule. It may give either (*a*) a pentose, (*b*) a tetrose, or (*c*) glyceraldehyde as the main reaction product. Other things being equal, reactions (*a*) and (*b*) will predominate. The pentose and tetrose which result from this oxidation may exist either as *aldehydo*-sugars or as ring structures. Should oxidation of the ring structure or lactol form occur, then a formic ester will be produced with a consequent lowering in the yield of titratable formic acid. On standing in water these esters will undergo hydrolysis and further oxidation, and a consequent slow rise in the titration figure will result. This formation of ester groupings from the oxidation of a lactol is small, since in no case have we encountered a yield of formic acid of less than 90% of the theoretical in our experiments on the oxidation of the sugar glycosides under the standardised conditions. In the oxidation of the reducing sugars, however, low yields of formic acid are produced when using our standardised reaction conditions. In certain instances, however, side reactions, with the formation of iodine, explain, in part, the low yields of formic acid produced in this complex oxidation reaction.

Experimental.

Oxidation with Sodium or Potassium Periodate. General Procedure.—Reactions were carried out in diffused light at 15—20° (with shaking when potassium periodate was used), in 500 c.c. stoppered bottles which had been cleaned with chromic acid and steamed out.

Sodium metaperiodate was prepared from sodium paraperiodate by recrystallisation from nitric acid. It contained no free acid since on addition of excess of ethylene glycol to its aqueous solution, sodium iodate neutral to methyl-red was formed. The ethylene glycol required was purified by distillation over solid potassium hydroxide. It was neutral to methyl-red.

The material (sufficient to give *ca.* 10 mg. of formic acid) was weighed out into a 500 c.c. stoppered bottle and dissolved or suspended in water. Excess of approximately 0·3M-sodium periodate was then added, followed by potassium chloride (5 g.) (if the oxidation was to be carried out with potassium periodate) and water to the requisite volume (usually 120 c.c.). Portions (either 10 or 20 c.c.) of the solution were withdrawn at intervals, excess of ethylene glycol was added to remove the residual periodate, and the formic acid was then determined either by titration with 0·01N-sodium hydroxide, using methyl-red as incidator, or after addition of potassium iodide by determination of the liberated iodine with 0·01N-thiosulphate. Blank experiments showed that under these conditions sodium iodate, formaldehyde, and ethylene glycol do not interfere with the estimation of formic acid and that the formic acid produced is not destroyed.

Oxidations with sodium metaperiodate. (1) α-Methylglucoside (87 mg.) was dissolved in water (115 c.c.), and sodium periodate solution (15 c.c.; 0·2M) was added. Portions of the solution (25 c.c.) were removed at intervals; ethylene glycol (approximately 0·1 c.c.) was added, and the formic acid titrated after a few minutes with 0·01N-sodium hydroxide. Titres: 6·3 c.c. (6 hours), 8·3 c.c. (22½ hours), 8·35 c.c. (47 hours), equivalent to 99·5% recovery.

After completion of oxidation a portion of the solution (50 c.c.) was extracted continuously with ether until the final extracts were neutral. The extracts were concentrated, and then required 18·8 c.c. of 0·01N-sodium hydroxide equivalent to 108% recovery of formic acid. The sodium formate obtained on evaporation of the neutralised solution gave, on heating with sulphuric acid (*d* 1·84) in a gas analysis apparatus, carbon monoxide corresponding to 99·4% of the theoretical yield of formic acid. The three different methods of determination gave reasonably concordant results, and the determination *via* carbon monoxide proves that the acid produced is formic acid.

(2) β-Methylmaltoside monohydrate (489·5 mg.) was dissolved in water (140 c.c.), and sodium periodate solution (60 c.c.; 0·275M) was added. The solution was left at 15—20°, samples (10 c.c.) were

withdrawn at intervals, ethylene glycol was added, and the solution titrated with 0·01N-barium hydroxide. At the same time the consumption of periodate and the change of optical rotation were determined.

Time (hours).	$[\alpha]_D^{19\cdot5°}$.	Formic acid produced (mols. per mol. of maltoside).	Consumption of periodate (mols. per sugar residue).
0	+176°	nil	nil
0·6	− 33	0·48	2·58
1·5	− 45	0·65	2·84
5·1	−100	0·89	2·97
30	− 62	1·19	3·61

The reaction was not finished after 30 hours, since formic acid continued to be produced. The last figure for formic acid (1·19 mols.) is considerably more than the theoretical value (1·0 mol.). High results were obtained also with other disaccharide derivatives, and the occurrence of over-oxidation even under carefully controlled conditions rendered the use of sodium periodate unsatisfactory for quantitative work, except when the reagent was employed in very slight excess.

Oxidations with potassium metaperiodate. (3) Mannitol was oxidised to show that formaldehyde and formic acid were unaffected by the oxidation conditions used above. The mannitol (28 mg.) was dissolved in water (110 c.c.) containing sodium periodate (11 c.c.; 0·236M) to which potassium chloride (5 g.) had been added. Titration of the liberated acid after addition of excess of glycol was made at intervals on portions of the solution. Found, mols. of formic acid per mol. of sugar: 3·56 (3 hours), 3·60 (98 hours), 3·80 (145 hours), 3·80 (194 hours), 3·88 (266 hours), 3·96 (338 hours), 3·96 (580 hours). Two other experiments gave similar results.

(4) α-Methyl-*d*-glucoside (81 mg.) was dissolved in water (110 c.c.) containing potassium chloride (5 g.), and sodium periodate (10 c.c.; 0·27M) was added. At intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol. of methylglucoside: 0·28 (1 hour), 0·43 (5½ hours), 0·69 (23 hours), 0·90 (51 hours), 0·91 (72 hours), 0·94 (170 hours), 0·97 (220 hours), 1·04 (460 hours).

(5) α-Methyl-*d*-galactopyranoside (111 mg.) was dissolved in water (110 c.c.), and potassium chloride (5 g.) and sodium periodate (10 c.c.; 0·236M) were added. The bottle and contents were then shaken and at intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol. of methylgalactoside: 0·95 (67 hours), 0·99 (120 hours), 1·01 (192 hours), 1·01 (230 hours), 1·03 (500 hours).

(6) α-Methyl-*d*-mannopyranoside (82 mg.) was dissolved in water (110 c.c.) containing potassium chloride (5 g.), and sodium periodate (10 c.c.; 0·282M) was added. The bottle and contents were shaken and at intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol. of methylmannoside: 0·67 (68 hours), 0·85 (121 hours), 0·93 (168 hours), 0·97 (211 hours), 0·95 (289 hours), 0·96 (405 hours).

(7) β-Methyl-*l*-arabopyranoside (89 mg.) was dissolved in water (110 c.c.) containing potassium chloride (5 g.), and sodium periodate (10 c.c.; 0·236M) was added. The bottle and contents were shaken and at intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol. of glycoside: 0·97 (47 hours), 0·99 (91 hours), 0·99 (143 hours), 1·01 (165 hours), 1·01 (215 hours), 1·02 (281 hours), 1·04 (362 hours), 0·99 (506 hours).

(8) α-Methyl-*d*-xylopyranoside (107 mg.) was oxidised as described for the oxidation of the arabinoside. Found, mols. of formic acid per mol. of glycoside: 0·71 (47 hours), 0·89 (91 hours), 0·93 (143 hours), 0·98 (165 hours), 0·98 (215 hours), 1·00 (287 hours), 1·02 (362 hours).

(9) β-Methylmaltoside monohydrate (249·7 mg.) was dissolved in water (70 c.c.) containing potassium chloride (2·5 g.), and sodium periodate solution (30 c.c., 0·275M) was then added. The whole was placed in a stoppered bottle which was continuously shaken. At intervals samples (10 c.c.) were withdrawn, and after addition of ethylene glycol the formic acid was titrated with 0·01N-barium hydroxide using methyl-red as indicator. Found, mols. of formic acid per mol. of maltoside: 0·13 (1¼ hours), 0·53 (20 hours); 0·75 (43 hours), 0·83 (66 hours), 0·92 (91 hours), 1·01 (163 hours); 1·03 (192 hours), followed by a very slow rise. One mol. of formic acid is liberated per mol. of maltoside in 150 hours.

(10) β-Methylcellobioside (106 mg.) was dissolved in water (110 c.c.) containing potassium chloride (5 g.), and sodium periodate (10 c.c., 0·28M) was added. At intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol of cellobioside: 0·69 (43 hours), 0·84 (91 hours), 0·87 (144 hours), 0·88 (185 hours), 0·89 (244 hours), 0·91 (291 hours).

(11) Amygdalin (173 mg.) was oxidised as described above (cf. Courtois and Valentino, *Bull. Soc. Chim. biol.*, 1944, **26**, 469). Found, mols. of formic acid per mol. of glycoside, 1·05 (47 hours), 1·28 (91 hours), 1·53 (143 hours), 1·83 (165 hours), 1·90 (215 hours), 2·03 (287 hours), 2·08 (362 hours), 2·00 (506 hours).

(12) Sucrose (111 mg.) was dissolved in water (105 c.c.) containing potassium chloride (5 g.), and sodium periodate (15 c.c.; 0·307M) was added. At intervals samples (20 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol. of sucrose: 0·84 (170 hours), 0·84 (195 hours), 0·92 (267 hours), 0·91 (315 hours), 0·91 (431 hours).

(12) Zinc borneol glucuronoside (110 mg.) was dissolved in water (105 c.c.) containing potassium chloride (5 g.), and sodium periodate (5 c.c., 0·285M) was added. At intervals samples (20 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol. of compound: 2·34 (162 hours), 1·74 (188 hours), 1·40 (210 hours), 1·06 (307 hours). The solution became brown owing to the separation of iodine and oily droplets of bornyl formate were observable.

(13) The methyl ester of α-methylgalacturonoside (21·95 mg.) was dissolved in water (200 c.c.) containing potassium chloride (5 g.), and sodium periodate (5 c.c., 0·308M) was added. At intervals samples (20 c.c.) were withdrawn and titrated. Found, mols. of formic acid per mol. of sugar: 0·22 (3 hours), 0·79 (25 hours), 1·23 (49 hours), 1·70 (74 hours), 2·18 (117 hours), 3·74 (171 hours), 4·22 (219 hours), 4·22 (335 hours).

(14) Lactose hydrate (94 mg.) was dissolved in water (100 c.c.) containing potassium chloride (5 g.)

and sodium periodate (20 c.c., 0·2M) was added. At intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of acid per mol. of lactose hydrate: 1·85 (42 hours), 2·87 (95 hours), 3·27 (142 hours), 3·68 (185 hours), 4·13 (263 hours), 2·41 (427 hours) (iodine was liberated at this stage with a resultant fall in acid titre).

(15) Lactal (160 mg.) was dissolved in water (100 c.c.) containing potassium chloride (5 g.) and sodium periodate (20 c.c.; 0·28M) was added. At intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of acid per mol. of lactal: 0·87 (42 hours), 1·00 (95 hours), 1·09 (142 hours), 1·17 (185 hours), 1·50 (263 hours), 2·06 (427 hours).

(16) α-Methyl-*d*-mannofuranoside (106 mg.) was dissolved in water (110 c.c.) containing potassium chloride (5 g.), and sodium periodate (10 c.c.; 0·236M) was added. At intervals samples (10 c.c.) were withdrawn and titrated. Found, mols. of acid per mol. of glycoside: 1·5 (47 hours), 2·0 (91 hours) (at this stage iodine began to be liberated and the alkali titre fell), 0·43 (143 hours) (all the periodate had then been converted into iodate and iodine).

(17) Oxalic acid dihydrate (27·02 mg.) was dissolved in water (115 c.c.) containing potassium chloride (5 g.), and sodium periodate solution (5 c.c.; 0·3072M) was added. At intervals samples were withdrawn and titrated. Found, mols. of oxalic acid: 0·43 (95 hours), 0·34 (120 hours), 0·31 (144 hours), 0·18 (430 hours), 0·12 (602 hours).

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270. *The Chloromethylation of Naphthalene and of Tetralin.*

By G. M. BADGER, J. W. COOK, and G. W. CROSBIE.

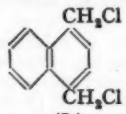
Chloromethylation of naphthalene with boiling aqueous formaldehyde and hydrochloric acid gives a mixture from which 1 : 4-bischloromethylnaphthalene and 1 : 5-*bischloromethylnaphthalene* have been isolated. From tetralin, 5 : 8-*bischloromethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* has been obtained.

FROM the products of the chloromethylation of 1-chloromethylnaphthalene, Anderson and Short (*J.*, 1933, 485) obtained a crude bischloromethylnaphthalene, m. p. 130—145°, which they were unable to purify. They regarded this as being largely the 1 : 5-derivative because, on reduction, they isolated and characterised 1 : 5-dimethylnaphthalene. Furthermore, on oxidation of the crude bischloromethylnaphthalene, they obtained the corresponding 1 : 5-dicarboxylic acid. Manske and Ledingham (*Canadian J. Res.*, 1939, **17**, 14) investigating the high-boiling residues resulting from Cambron's (*ibid.*, p. 10) chloromethylation of naphthalene, obtained a supposedly pure bischloromethylnaphthalene, m. p. 144°, which they regarded as the 1 : 5-derivative. Evidence for this was obtained by conversion into the dinitrile, hydrolysis to the diacetic acid, and decarboxylation to dimethylnaphthalene. The hydrocarbon was an oil, giving a picrate, m. p. 138°. As 1 : 5-dimethylnaphthalene is a solid, and as the picrates of the 1 : 5- and 1 : 4-dimethylnaphthalenes have closely similar melting points, this evidence was inconclusive.

However, supposing the major product of the bischloromethylation of naphthalene to be the 1 : 5-derivative, we decided to attempt the synthesis of *s*-hexahydropyrene by condensing bischloromethylnaphthalene with ethyl malonate, followed by hydrolysis, decarboxylation, ring-closure and reduction. While this work was in progress, two papers by Lock and Walter (*Ber.*, 1942, **75**, 1158; 1944, **77**, 286) became available to us, and we found that the main object of our work had already been achieved. In the second paper, these authors state that the bischloromethylnaphthalene, for which they give m. p. 150°, is not the 1 : 5- but the 1 : 4-derivative; no evidence of this was presented. Our work has confirmed this conclusion of Lock and Walter, and we have also isolated the 1 : 5-derivative from the crude bischloromethylnaphthalenes resulting from the chloromethylation both of naphthalene and of 1-chloromethylnaphthalene.

Naphthalene was chloromethylated with boiling aqueous formaldehyde and hydrochloric acid (B.P. 345,146; Lock and Walter, *loc. cit.*). Taking advantage of solubility differences in ether, the crude product was separated into several fractions, from which 1 : 5-*bischloromethylnaphthalene* (II), m. p. 172°, and 1 : 4-bischloromethylnaphthalene (I), m. p. 150°, were obtained by repeated recrystallisation. The constitution of each product was shown by reduction to the dimethylnaphthalene, which was characterised by the formation of the picrate and *s*-trinitrobenzene complex. The major mixed fraction resulting from the treatment with ether had m. p. 128—130°. That this contained some 1 : 5-bischloromethylnaphthalene was

shown by the isolation, in poor yield, of crystalline 1 : 5-dimethylnaphthalene after reduction, a result which is in agreement with the work of Anderson and Short (*loc. cit.*). However, that this fraction consisted largely of the 1 : 4-isomer was shown by its conversion into 1 : 4-bis-(ωω-dicarbethoxyethyl)naphthalene (III) (Lock and Walter, *loc. cit.*). The constitution of this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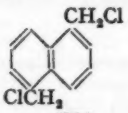
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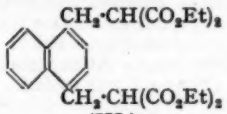
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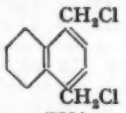
(IV.)

product was shown by hydrolysis, followed by oxidation with potassium ferricyanide, to naphthalene-1 : 4-dicarboxylic acid. 1 : 4-Bischloromethylnaphthalene has also been converted into the corresponding dinitrile. This appears to be the same as the dinitrile described as the 1 : 5-derivative by Manske and Ledingham (*loc. cit.*), and we therefore believe that these authors were in error in attributing the 1 : 5-configuration to their products, which should all be described as 1 : 4-derivatives. To confirm this conclusion we have also prepared *naphthalene-1 : 5-diacetonitrile* from pure 1 : 5-bischloromethylnaphthalene.

The patent literature (D.R.-P. 533,850) describes the preparation of a bischloromethyltetralin. We have also prepared this, and have shown that it is *5 : 8-bischloromethyl-1 : 2 : 3 : 4-tetrahydronaphthalene* (IV). Reduction with zinc and hydrochloric acid, or with hydrogen and palladium, gave 5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which on dehydrogenation with sulphur, or with palladised asbestos, gave 1 : 4-dimethylnaphthalene, characterised by the formation of the picrate and *s*-trinitrobenzene complex.

Experimental.

Chloromethylation of Naphthalene.—(*a*) A mixture of naphthalene (80 g.), aqueous formaldehyde (40%; 220 g.), and concentrated hydrochloric acid (220 g.) was boiled under reflux with vigorous stirring for 16 hours, while a current of hydrogen chloride was introduced through a tube leading to the bottom of the flask. After cooling, the aqueous layer was decanted, and the pasty mass triturated with ether (100 c.c.). In one run, this ethereal solution deposited, on standing, 1 : 4-bischloromethylnaphthalene (30 mg.) as colourless needles from alcohol, m. p. 149—150° (Found : C, 64·1; H, 4·5. Calc. for $C_{12}H_{10}Cl_2$: C, 64·0; H, 4·4%). This compound was later obtained pure in considerable quantity. The ethereal solution, after evaporation, gave 1-chloromethylnaphthalene (43 g.), b. p. 150—152°/13 mm., and crude bischloromethylnaphthalenes, b. p. 180—200°/13 mm., m. p. 128—130°.

The solid obtained after this ether washing was extracted with ether (200 c.c.) in a Soxhlet apparatus. The ether deposited, on cooling, crude bischloromethylnaphthalene (19 g.), m. p. 128—130°. Recrystallisation from alcohol did not raise the m. p., although later work showed that this fraction contained both the 1 : 4- and the 1 : 5-isomer. The ethereal filtrate, on evaporation, gave a further impure fraction, m. p. 105—115° (2 g.). The residue (4·0 g.), m. p. 153—159°, remaining in the Soxhlet thimble gave, after several recrystallisations from alcohol, colourless needles of 1 : 5-*bischloromethylnaphthalene*, m. p. 171·5—172·5° (Found : C, 64·0; H, 4·4. $C_{12}H_{10}Cl_2$ requires C, 64·0; H, 4·4%).

The above experiment was successfully repeated several times, but in two large scale runs naphthalene (700 g.) gave crude bischloromethylnaphthalene (300 g.) from which no pure 1 : 5-bischloromethylnaphthalene could be isolated by the above procedure. The crude product was soluble in ether (500 c.c.) and, after several recrystallisations, gave pure 1 : 4-bischloromethylnaphthalene.

(*b*) Crude bischloromethylnaphthalene was also obtained by chloromethylating 1-chloromethylnaphthalene (250 g.) in light petroleum (b. p. 100—120°; 300 c.c.) with paraformaldehyde (60 g.) and anhydrous zinc chloride (15 g.), by the method of Anderson and Short, except that the reaction was carried out on the steam-bath, and that hydrogen chloride was passed for 24 hours. The product, obtained in *ca.* 60% yield, was separated as above, and gave 1·5 g. of pure 1 : 5-bischloromethylnaphthalene, m. p. 171·5—172·5°.

Reduction of fraction, m. p. 128—130°. A mixture of bischloromethylnaphthalene, m. p. 128—130° (1·2 g.), in a little alcohol, and zinc dust (1·5 g.) was boiled for 1 hour, concentrated hydrochloric acid being added at intervals. After distillation (b. p. 60—65°/0·2 mm.), the product was dissolved in 50% acetone. After standing, the crystalline product which separated (75 mg.) was recrystallised from alcohol, and had m. p. 79·5—80·5°. The orange-red picrate had m. p. 138—139°, and the product isolated was therefore 1 : 5-dimethylnaphthalene, in agreement with Anderson and Short (*loc. cit.*).

Reduction of 1 : 4-*bischloromethylnaphthalene.* 1 : 4-Bischloromethylnaphthalene (m. p. 149°) was reduced in about 50% yield as above. The product formed a colourless oil, b. p. 132—134°/15 mm. (Found : C, 92·4; H, 7·4. Calc. for $C_{12}H_{12}$: C, 92·3; H, 7·7%). The picrate crystallised from methanol in long orange-red needles, m. p. 142—144° (Found : N, 10·9. Calc. for $C_{18}H_{15}O_7N_3$: N, 10·9%); Kloetzel (*J. Amer. Chem. Soc.*, 1940, **62**, 1708) gives m. p. 143—144°. The *s*-trinitrobenzene complex formed yellow needles, from methanol, m. p. 164—166° (Found : N, 11·6. Calc. for $C_{18}H_{15}O_6N_3$: N, 11·4%); Kloetzel (*loc. cit.*) gives m. p. 165—166°. The reduction product was therefore 1 : 4-dimethylnaphthalene.

The reduction was also carried out in almost quantitative yield by hydrogenation over palladium black in acetone.

Reduction of 1 : 5-*bischloromethylnaphthalene.* 1 : 5-Bischloromethylnaphthalene (m. p. 172°) was reduced as above with zinc and hydrochloric acid. The 1 : 5-dimethylnaphthalene, which crystallised

from the reaction mixture, was purified by sublimation at 100°/13 mm., and formed colourless lustrous plates, m. p. 80—81° (Found: C, 92·2; H, 7·6. Calc. for $C_{12}H_{12}$: C, 92·3; H, 7·7%); Butz (*J. Amer. Chem. Soc.*, 1940, **62**, 2557) gives m. p. 80°, and Anderson and Short (*loc. cit.*) give m. p. 80—80·5°. The picrate formed orange-red needles, from methanol, m. p. 138—139° (Found: N, 10·9. Calc. for $C_{18}H_{15}O_7N_3$: N, 10·9%); Butz (*loc. cit.*) gives m. p. 137°, and Anderson and Short (*loc. cit.*) give m. p. 138—139°. The *s-trinitrobenzene* complex formed yellow needles, from alcohol, m. p. 158—159° (Found: N, 11·3. $C_{18}H_{15}O_6N_3$ requires N, 11·4%).

1 : 4-*Bis*-(*ωω-dicarboxyethyl*)*naphthalene*.—Ethyl malonate (200 g.) was added to a solution of sodium (18 g.) in alcohol (300 c.c.). After cooling, bischloromethylnaphthalene, m. p. 128—130° (23 g.), suspended in alcohol (200 c.c.) was added. After 10 hours' refluxing the product was worked up in the usual way. The ester (20 g.) formed colourless needles, from alcohol, m. p. 68·5—69° (Found: C, 65·8; H, 6·7. Calc. for $C_{24}H_{32}O_8$: C, 66·1; H, 6·8%); Lock and Walter (*loc. cit.*) give m. p. 66·5°. A solution of this ester (20 g.) in methanol (75 c.c.), water (150 c.c.), and sodium hydroxide (36 g.) was refluxed for 8 hours, a further quantity (10 g.) of sodium hydroxide being added after the first 4 hours. The bismalonic acid (9 g.) was recrystallised from water. It decomposed at about 140° with evolution of gas, finally melting at 255—256°.

Proof of constitution. A solution of this acid (2 g.), potassium ferricyanide (300 g.), potassium hydroxide (43 g.), and water (1 l.) was heated at 70—80°, with stirring, for 24 hours. A further quantity (80 g.) of potassium ferricyanide and potassium hydroxide (14 g.) in a little water was then added, and the heating continued for 8 hours. After cooling, the filtered solution was acidified, and the precipitate collected, suspended in water, and extracted with ether. The ethereal extract on evaporation gave an acid, m. p. 309—310° (75 mg.). The methyl ester had m. p. 63—64°. These constants are in agreement with the published figures for naphthalene-1 : 4-dicarboxylic acid.

Naphthalene-1 : 4-*diacetonitrile*.—The following procedure was found superior to that of Manske and Ledingham (*loc. cit.*). A mixture of 1 : 4-bischloromethylnaphthalene, m. p. 148—150° (0·5 g.), potassium cyanide (0·5 g.) in a little water, and alcohol (30 c.c.) was boiled under reflux for 2 hours. After addition of water, the naphthalene-1 : 4-diacetonitrile (0·3 g.) was recrystallised from alcohol, and formed colourless prisms, m. p. 140—142° (Found: C, 81·7; H, 4·75. Calc. for $C_{14}H_{10}N_2$: C, 81·55; H, 4·85%). The same compound was obtained following a similar experiment with crude bischloromethylnaphthalene, m. p. 128—130°. This compound is evidently identical with the derivative, m. p. 140°, described by Manske and Ledingham (*loc. cit.*) as the 1 : 5-derivative.

Naphthalene-1 : 5-*diacetonitrile*.—This was prepared as above, using 1 : 5-bischloromethylnaphthalene. The *naphthalene*-1 : 5-*diacetonitrile* formed colourless small needles, m. p. 188—189° (Found: C, 81·4; H, 4·6. $C_{14}H_{10}N_2$ requires C, 81·55; H, 4·85%).

Chloromethylation of Tetralin.—Freshly distilled tetralin (90 g.), concentrated hydrochloric acid (210 g.), and aqueous formaldehyde (40%; 220 g.) were boiled under reflux, with stirring, for 48 hours, while hydrogen chloride was passed in. The cooled mixture was extracted with ether, and the ethereal solution dried and evaporated. The oily residue partly crystallised. The solid was collected, washed with a little ether, and recrystallised from alcohol. 5 : 8-*Bischloromethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (10 g.) was obtained as colourless lustrous needles, m. p. 117—118° (Found: C, 62·9; H, 6·0. $C_{12}H_{14}Cl_2$ requires C, 62·9; H, 6·1%). The oil was collected in two fractions, b. p. 150—180°/17 mm. (65 g.), and 180—195°/13 mm. (12 g.). The latter deposited a further quantity (2 g.) of bischloromethyltetralin on standing.

5 : 8-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. 5 : 8-Bischloromethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (4·5 g.) was reduced with zinc and hydrochloric acid, in alcohol, as described for the bischloromethylnaphthalenes. The 5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (0·8 g.) was obtained as a colourless oil, b. p. 125°/14 mm. (Found: C, 90·1; H, 10·25. Calc. for $C_{12}H_{16}$: C, 90·0; H, 10·0%) (cf. Barnett and Sanders, *J.*, 1933, 434). The reduction was also carried out, in almost quantitative yield, by hydrogenation over palladium black in acetone.

Dehydrogenation of 5 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The above dimethyltetrahydronaphthalene (0·5 g.) was dehydrogenated with sulphur (0·3 g.) at 230—250° for 2 hours. The product was converted into the picrate (0·6 g.), which formed orange-red needles, m. p. 142—143°, alone, or mixed with the picrate of 1 : 4-dimethylnaphthalene. The *s*-trinitrobenzene complex formed yellow needles, m. p. 163—165°, alone, or mixed with the *s*-trinitrobenzene complex of 1 : 4-dimethylnaphthalene. The same results were obtained when the dehydrogenation was carried out with palladised asbestos at 240° for 5 hours.

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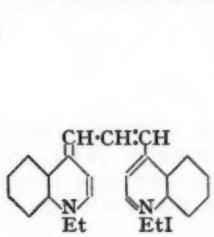
271. *Some Trinuclear Cyanine Dyes. Part I. The Synthesis of Neocyanines.*

By FRANCES M. HAMER, RUSSELL J. RATHBONE, and BARBARA S. WINTON.

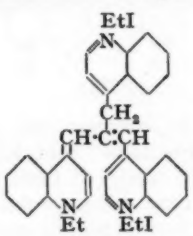
Neocyanine is a trinuclear cyanine dye, which had been obtained as a by-product by the action of alkali on a lepidinium salt in the presence of iodoform or ethyl orthoformate, and for which three formulæ had been proposed. That which represents it as being both a substituted trimethincyanine and a substituted pentamethincyanine has now been established by synthesis. Analogous dyes having three similar heterocyclic nuclei other than 4-linked quinoline have also

been synthesised. The necessary branched-chain intermediates, consisting of *N*-alkyldihydro-derivatives of heterocyclic bases, with a dianilo*iso*propylidene group in the reactive position, were prepared from the corresponding methylene bases or their anilomethyl derivatives, by heating with ethyl*iso*formanilide and zinc chloride. Their condensation with heterocyclic quaternary ammonium salts, having a reactive methyl group, resulted in neocyanines identical with those obtained empirically, when such existed. The absorption maxima of the trinuclear dyes have been compared with those of the related tri- and penta-methincyanines.

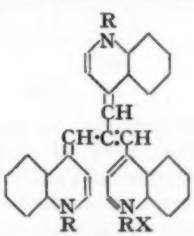
NEOCYANINE, a new sensitiser for the infra-red, was announced by Dundon, Schoen, and Briggs (*J. Opt. Soc. Amer.*, 1926, **12**, 397) as sensitising more powerfully beyond 8000 A. than any dye previously reported. They said it had been isolated by H. T. Clarke as a less soluble by-product in the preparation of 4 : 4′-carbocyanine but did not specify his method. At that time, the normal method for preparing a 4 : 4′-carbocyanine, apart from the synthesis by Mills and Braunholtz which established its constitution (I) (*J.*, 1923, **123**, 2804), consisted in treating a lepidinium salt with alkali in the presence of formaldehyde or chloroform (Adams and Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661). Only in 1928 did the acceptance of a British patent disclose that neocyanine had been produced in a 4 : 4′-carbocyanine preparation in which iodoform had been used instead (Kodak Ltd., B.P. 292,274/1927); the corresponding American patent did not appear for another three years (Clarke, U.S.P. 1,804,674/1931). Meanwhile one of us (Hamer, *J.*, 1927, 2796), in describing a general method for the preparation of carbocyanines by condensing a quaternary, heterocyclic ammonium salt having a reactive methyl group, with ethyl orthoformate in the presence of pyridine, recorded that the 4 : 4′-carbocyanine was accompanied by a by-product, identical with neocyanine. Soon afterwards, in preparing a neocyanine from each of three lepidinium salts, a modified method gave 36—41% yields. Analyses led to the conclusion that the neocyanine molecule had been formed from three molecules of lepidine alkyl halide, with elimination of hydrogen halide, and that either one or two



(I.)



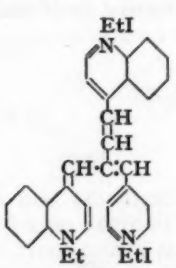
(II.)



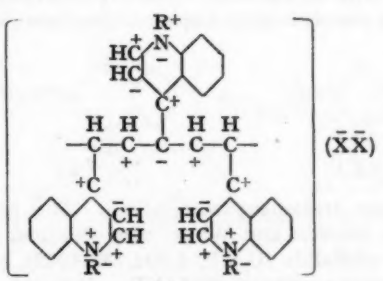
(III.)

additional carbon atoms had entered the molecule. Based on the former supposition, the first neocyanine formula (II), showing it as a β-substituted 4 : 4′-carbocyanine (I), was proposed (Hamer, *J.*, 1928, 1472).

To dyes prepared from lepidinium and from quinaldinium salts, with carbon tetrachloride and alkali, Ogata and Tamura assigned formulæ such as (III) (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 475), but Ogata subsequently disclaimed these (*ibid.*, p. 491) and adopted formulæ of type (II) for dyes of the neocyanine class, which he prepared from alkiodides of several heterocyclic bases with orthoformic ester or diphenylformamidine in the presence of various condensing agents (*Proc. Imp. Acad. Tokyo*, 1932, **8**, 503; *ibid.*, 1933, **9**, 602; *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 497).



(IV.)



(V.)

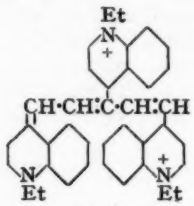
In 1931 Brooker described the neocyanines of the thiazole series and in addition to a formula of type (II) suggested an alternative (IV) with a different carbon chain (B.P. 408,273/1931).

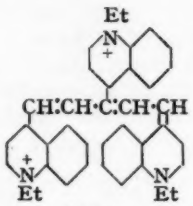
Since alkali would be likely to convert (II) into (III), whereas (IV) had the advantage of explaining the stability of the neocyanines to alkali, formula (IV) was preferred to (II) (Brooker, Hamer, and Mees, *Phot. J.*, **1933, 57, 258**; *J. Opt. Soc. Amer.*, **1933, 23, 216**).

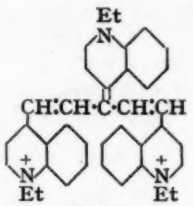
In 1935 W. König, in a theoretical paper on the chemistry of sensitisers, expressed his disbelief in formula (II) and said that he regarded neocyanine as a pentamethincyanine of formula (V). He pointed out that whereas (V) has 4 : 4′-linkings, other analogous substances with 2 : 2′-linkings are also possible, and he gave a general formula for those (*Z. wiss. Phot.*, **1935, 34, 15**).

The essential feature of König's formula was the symmetrical attachment of the three heterocylcic nuclei to an unbranched pentamethin chain, and concurrence with this view of the structure was at once expressed (Hamer, *Chem. and Ind.*, **1935, 13**, 640) on the ground that it accorded with a reasonable manner of formation of the dye; neocyanine could be regarded as arising from the condensation of the methyl group of lepidine ethiodide with two molecules of ethyl orthoformate and the subsequent condensation of the resulting intermediate with two more molecules of lepidine ethiodide.

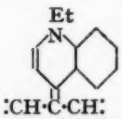
On the modern views a neocyanine kation of this structure would have its two units of positive charge distributed over the three basic groups. It cannot therefore be represented by a single structural formula, but would be regarded as a resonance hybrid of the three canonical structures (VI*a*, *b*, and *c*).

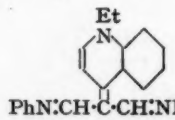

(VI*a*.)


(VI*b*.)

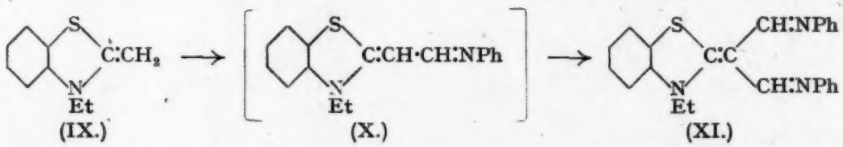

(VI*c*.)

These formulæ, in particular (VI*c*), suggest the possibility of a rational synthesis of neocyanine from a suitable intermediate containing the grouping (VII), and the dianilo-compound (VIII) seemed most likely to fulfil this purpose. We have succeeded in preparing a number of dianils of this type and have found that with their aid the synthesis of the corresponding neocyanines can in fact be readily accomplished.

(VII.) 

 (VIII.)

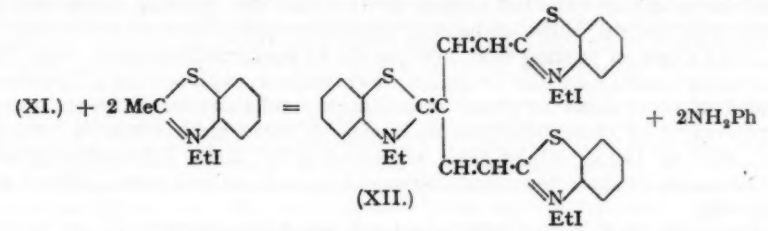
The synthesis was first carried out in the benzthiazole series, with the aid of ethyl*iso*formanilide which, as Knott has recently shown (*J.*, **1946**, 120), condenses even more readily than diphenylformamidine (I.C.I. Ltd., Piggott, and Rodd, B.P. 344,409/1929) with pyridinium salts having a reactive methyl group. As a starting point we employed, instead of a quaternary salt, the methylene base 3-ethyl-2-methylenebenzthiazoline (IX) (Hamer, Rathbone, and Winton, this vol., p. 954). Heated with ethyl*iso*formanilide in the presence of zinc chloride, this yielded a zinc chloride complex of the base (XI), from which the *base* itself could be isolated


(IX.) (X.) (XI.)

by appropriate treatment with alkali. The presumed intermediate (X) had already been described by Brooker and White, who obtained it by the action of alkali on 2-β-anilinovinylbenzthiazole ethiodide (U.S.P. 2,298,732/1942), and we found that it also could be condensed with ethyl*iso*formanilide to yield (XI). It is safe to assume that the methin group attached to the ring is attacked, rather than the more remote methin group, since the former is in the well-known reactive position. We should have liked to have obtained direct proof of this assumption and therefore prepared the α- and β-methyl derivatives of (X) (Hamer, Rathbone,

and Winton, *loc. cit.*), hoping to be able to condense the β-methyl derivative with ethyl*iso*formanilide, but the attempt, as also that with the α-methyl derivative, was unsuccessful.

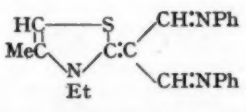
The final stage in the synthesis was readily effected. The dianilo-base (XI), heated for a few minutes with 2-methylbenzthiazole ethiodide, either in pyridine solution or with sodium acetate and acetic anhydride, gave in excellent yield a neocyanine (XII), identical with that obtained by Ogata's method (*Proc. Imp. Acad. Tokyo*, 1933, **9**, 602; *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 497) from a 2-methylbenzthiazolium salt and ethyl orthoformate.



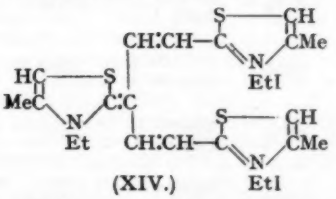
(XII.)

In the thiazole series we prepared the *dianilo-base* (XIII) from 4-methyl-3-ethyl-2-anilo-ethylidene-Δ^4-thiazoline, condensed it with 2 : 4-dimethylthiazole etho-*p*-toluenesulphonate in pyridine, and isolated the dye as iodide (XIV), which was identical with that obtained by the empirical method from the same quaternary salt with ethyl orthoformate and pyridine (B.P. 408,273/1931).

Neocyanine itself was synthesised in a similar manner. The necessary *dianil* (VIII) was prepared by condensation of the methylene base from lepidine etho-*p*-toluenesulphonate with ethyl*iso*formanilide and this, heated with lepidine ethiodide, acetic anhydride and sodium acetate,



(XIII.)

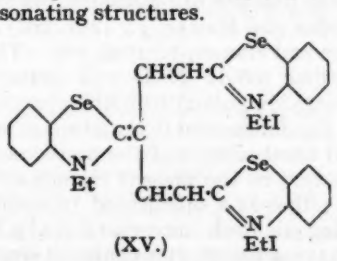


(XIV.)

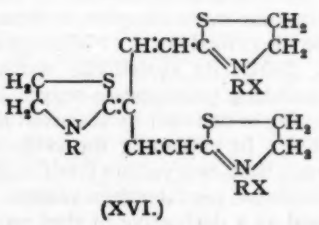
gave in 20% yield a product identical with the neocyanine obtained from lepidine ethiodide and ethyl orthoformate in the presence of pyridine (Hamer, *J.*, 1927, 2796; cf. *idem*, *J.*, 1928, 1472).

The synthesis of neocyanines in this manner may be taken as proof of the correctness of the structure now assigned to them.

In addition to the three dianilo-bases, (VIII), (XI), and (XIII), the following representatives of this class have been prepared : *5-chloro-3-ethyl-2-dianiloisopropylidenebenzthiazoline*, *3-ethyl-2-dianiloisopropylidene-6 : 7-benzbenzthiazoline*, *3-ethyl-2-dianiloisopropylidenebenzselenazoline*, *3-methyl-2-dianiloisopropylidenethiazolidine*, *3-ethyl-2-dianiloisopropylidenethiazolidine*, *1-ethyl-2-dianiloisopropylidene-1 : 2-dihydroquinoline*, *3-ethyl-2-dianiloisopropylidenebenzoxazoline*. From the dianils, new neocyanines were prepared, namely the *dichloride* corresponding with the di-iodide (XII), *analogues* of (XII) having, respectively, three 6 : 7-benzbenzthiazole and three 5-chlorobenzthiazole nuclei, its *selena*-analogue (XV), and two Δ^2-*thiazoline* analogues (XVI). It will naturally be understood that each of these formulæ is to be taken as the representative of a set of resonating structures.



(XV.)



(XVI.)

The absorption curves of methyl-alcoholic solutions of the trinuclear dyes were plotted. They were well-defined and rather narrow, with sometimes an inflexion on the short wave-length side. Since the neocyanines might be regarded as combining the structural characters of the

tri- and penta-methincyanines, we give in the following table the wave-lengths of the absorption maxima of seven neocyanines and for comparison those of the corresponding tri- and penta-methincyanines. Certain abbreviations, obvious in conjunction with the text, have been used. Each previously recorded absorption maximum is marked with a bibliographic reference, the unmarked ones being those of compounds described in the present paper. Some of the parent cyanines were prepared for the sake of this comparison. With each of the seven neocyanines, the absorption maximum lies between that of the unsubstituted trimethincyanine and pentamethincyanine, as recorded already for one such dye (Hamer, *Chem. and Ind.*, 1935, **13**, 640). The bathochromic shifts on passing from trimethincyanine to neocyanine vary from 375 to 710 A. and those on passing from neocyanine to pentamethincyanine vary from 350 to 520 A. Other comparisons may also be made. For instance, replacement of the three 4-linked quinoline nuclei of neocyanine by three benzthiazole nuclei caused a hypsochromic shift of 1735 A. Replacement of three benzthiazole nuclei by three methylthiazole nuclei caused a hypsochromic shift of 140 A., whilst their replacement by three 5-chlorobenzthiazole, three 6 : 7-benzbenzthiazole, or three benzselenazole nuclei caused bathochromic shifts of 90,335, and 185 A., respectively.

The new dyes comprised photographic sensitisers and desensitisers.

Neocyanine.	Abs. max., A.	Trimethincyanine.	Abs. max., A.	Pentamethincyanine.	Abs. max., A.	Bathochromic shifts: trimethin- to neocyanine.	Bathochromic shifts: neo- to pentamethincyanine.
4–q, 4–q, 4–q (VI)	7750 *	4–q, 4–q (I)	7040 †	4–q, 4–q	8100 †	710	350
bzth, bzth, bzth (XII)	6015	bzth, bzth	5570 †	bzth, bzth	6500 †	445	485
bzbzth, bzbzth, bzbzth	6350	bzbzth, bzbzth	5930 †	bzbzth, bzbzth	6870 †	420	520
Clbzth, Clbzth, Clbzth	6105	Clbzth, Clbzth	5625 ‡	Clbzth, Clbzth	6560	480	455
bzSe, bzSe, bzSe (XV)	6200	bzSe, bzSe	5700 †	bzSe, bzSe	6600 †	500	400
Me–th, Me–th, Me–th (XIV)	5875	Me–th, Me–th	5520 §	Me–th, Me–th	6370	375	495
thiazoline, thiazoline, thiazoline (XVI; R = Et, X = ClO_4)	5060	thiazoline, thiazoline	4435 ‖	thiazoline, thiazoline	5450	625	390

* Hamer, *Chem. and Ind.*, 1935, **13**, 640.
† Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703.
‡ Hamer, Rathbone, and Winton, this vol., p. 954.
§ Cf. Fisher and Hamer, *J.*, 1930, 2502.
‖ Brooker, *J. Amer. Chem. Soc.*, 1936, **58**, 662.

Nomenclature.—Some years ago we first adopted the practice of publishing the systematic names for the cyanines in addition to other names (Fisher and Hamer, *J.*, 1937, 907) or, as the structures became more complex, exclusively (Beilenson and Hamer, J., 1942, 98). Thus whilst (I) may be described as 1 : 1′-diethyl-4 : 4′-carbocyanine iodide (Mills and Braunholtz, *J.*, 1923, **123**, 2804), its systematic name is [bis-4-(1-ethylquinoline)]trimethincyanine iodide. This nomenclature presupposes only a knowledge of the fundamental structure of a cyanine dye; each ring is denoted by its usual description and numbering, and the positions of linking are indicated. In extending the systematic nomenclature to the present trinuclear cyanines, it is apparent that neocyanine itself might be named either as a substituted trimethincyanine or as a substituted pentamethincyanine. In introducing one fresh convention, that a trinuclear dye is named as a derivative of that parent cyanine having the shorter chain, of course we do not intend to imply that it actually is a derivative of that cyanine rather than of the one having the longer chain. A second parenthesis is introduced to comprise the third nucleus and here the numbers which indicate the position of linking and the positions of substituents are each

followed by a dash, whilst the Greek letters show the positions of attachment of the chain linking the third nucleus. Thus neocyanine is called [bis-4-(1-ethylquinoline)][αβ′-dimethin-4′-(1′-ethylquinoline)]trimethincyanine di-iodide.

Experimental.

3-Ethyl-2-dianiloisopropylidenebenzthiazoline (XI).—3-Ethyl-2-methylenebenzthiazoline (33·17 g.; 1 mol.), zinc chloride powder (76·5 g.; 3 mols.), and ethyl*iso*formanilide (277 c.c.; 10 mols.) were heated together at 175—180° for 2½ hours, with mechanical stirring. Acetone (700 c.c.) was added, and the mixture heated until all lumps had gone. After cooling, the zinc chloride complex was filtered off and washed with acetone. It was ground with, and stirred into, water (750 c.c.). It was filtered off, washed with methyl alcohol, boiled out twice with that solvent (1000 c.c., 200 c.c.), and washed twice with hot methyl alcohol (50 c.c. × 2).

For converting the complex (54·2 g.) into base, it was ground with water (10 c.c. per g.) and with 40% sodium hydroxide solution (20 c.c. per g.) and the suspension was shaken with acetone (100 c.c. per g.). The acetone extract was filtered and the aqueous residue was further extracted twice with acetone (10 c.c. per g. × 2). The extracts were dried over stick sodium hydroxide for a period of days, then filtered, and the acetone was distilled off under a vacuum (in six lots) and the concentrate (volume about 15 c.c. × 6) cooled. The *base* crystallised and was filtered off and washed with methyl alcohol until the washings were no longer brown. The yield was 28% (19·76 g.). In recrystallising from methyl alcohol (110 c.c. per g.), the time of heating was kept to a minimum and the yield was 21% (15·36 g.). (After drying in a vacuum desiccator, it was analysed by the method of Carius, which method was used throughout this work for sulphur and halogen determinations.) (Found: S, 7·9. Found, after a second recrystallisation: S, 8·2. $C_{24}H_{21}N_3S$ requires S, 8·35%). The yellow crystals had m. p. 127°, becoming orange at about 110°. The broad absorption curve had its maximum at 4020 A. and an inflexion at 3500 A. The base was photographically inert.

In the second method of preparation, 3-ethyl-2-aniloethylidenebenzthiazoline (X) (47 g.; 1 mol.), zinc chloride (94 g.; 4·1 mols.), and ethyl*iso*formanilide (250 g.; 10 mols.) were heated together at 160—185° for 1 hour. After partial cooling, acetone (1000 c.c.) was added; refluxing was applied, in order to break up a hard lump. When cold, the solid was filtered off, washed with acetone, and ground with water (107 g. obtained). It was thrice boiled out with methyl alcohol (2350 c.c. × 3) (8·01 g., 0·09 g., and 0·16 g., respectively, crystallised from the filtrates). When a test portion of the solid from the first boiling out was heated with a 2-methylbenzthiazolium salt in pyridine, it gave a red colour, whilst a test portion of the second or third, when similarly treated, gave a blue. The boiling out with methyl alcohol halved the weight of zinc chloride complex. It was converted into free base as before and gave a 17% yield (11 g.), and after recrystallisation from methyl alcohol 10% (6·46 g.). Its m. p. was the same as that of the sample prepared by the first method, and that of the mixture was identical.

5-Chloro-3-ethyl-2-dianiloisopropylidenebenzthiazoline.—5-Chloro-3-ethyl-2-methylenebenzthiazoline (24 g.; 1 mol.), zinc chloride (47 g.; 3 mols.), and ethyl*iso*formanilide (170 g.; 10 mols.) were heated together at 190°, with mechanical stirring, for 1½ hours. After partial cooling, acetone (1000 c.c.) was added and the solid was filtered off, ground with water (28 g. left), and boiled out with methyl alcohol (500 c.c. × 4). The filtrates varied from purple to pale pink, but a negligible amount of solid (total, 0·1 g.) separated from them. The yellow zinc chloride complex (24·12 g.) was ground with 40% sodium hydroxide solution (400 c.c.) and water (200 c.c.) and extracted with acetone (5000 c.c.). The extract was dried with stick sodium hydroxide, the solvent distilled off under a vacuum, and the concentrate cooled, giving a 16% yield of crude *base* (7·83 g.). A sample was recrystallised from pyridine (5 c.c. per g.; yield 12%) (Found, after drying in a vacuum at 60—80°, which method of drying was employed throughout this work except where otherwise stated: Cl, 8·7. $C_{24}H_{20}N_3ClS$ requires Cl, 8·5%). The yellow crystals had m. p. 182—184°. The absorption curve had its maximum at 4100 A. and tailed off very gradually on the short wave-length side. Towards a gelatino-chloride photographic emulsion the substance exerted slight sensitisation as far as 4700 A.

3-Ethyl-2-dianiloisopropylidene-6:7-benzbenzthiazoline.—To 3-ethyl-2-methylene-6:7-benzbenzthiazoline (11·43 g.) was added ethyl*iso*formanilide; zinc chloride powder was stirred in, and the mixture heated. It was stirred by hand, in order to break up the lumps of zinc chloride, until the oil-bath temperature reached 80°. Mechanical stirring was then applied and the temperature was raised to 175—180° and held there for an hour. After cooling, the hard reaction product was treated with acetone (250 c.c.), being heated and stirred at intervals for a few hours in order to break up the lumps. The solid was filtered off, washed with acetone, ground with water, and then boiled out four times with methyl alcohol (450 c.c. × 4). The residual complex (9·52 g.) was ground with water (10 c.c. per g.), added to acetone (100 c.c. per g.), and shaken with 40% sodium hydroxide solution (20 c.c. per g.) until all solid had disappeared. The acetone layer was filtered, and the aqueous part further twice extracted with acetone (200 c.c., 100 c.c.). The extracts were dried over stick sodium hydroxide for 2 days. The filtrate was then concentrated under a vacuum until almost all the acetone had been removed and only a little aqueous liquid was left. The solid which separated on cooling was filtered off and obtained, after washing with acetone, in 21% yield (4·49 g.). It was recrystallised from methyl alcohol (4000 c.c.), the time of heating being reduced to the very minimum. The yield was 9% (1·86 g.) but in a recrystallisation where boiling with mechanical stirring went on for 7 minutes the yield was only half that (Found: S, 7·2. $C_{28}H_{23}N_3S$ requires S, 7·4%). The dull yellow crystals melted at about 173° with previous darkening and shrinking. The absorption maximum was at 3890 A. and the *base* did not sensitise a gelatino-chloride photographic emulsion.

3-Ethyl-2-dianiloisopropylidenebenzselenazoline.—3-Ethyl-2-aniloethylidenebenzselenazoline (20 g.; 1 mol.), ethyl*iso*formanilide (44 g.; 5 mols.), and zinc chloride (18 g.; 2·2 mols.) were heated together at 160—170° for 30 minutes. The product was treated with water, and the solid was next thoroughly ground and washed with acetone and boiled out with methyl alcohol (1400 c.c.). The zinc chloride

complex (11·5 g.) was converted into base, by grinding to a paste with water and shaking with 40% sodium hydroxide solution (100 c.c.) and acetone (500 c.c.). The filtered acetone extract was dried with stick sodium hydroxide, then concentrated considerably. The *base* was filtered off, washed with spirit, and obtained in 14% yield (3·8 g.). On recrystallisation from methyl alcohol (80 c.c. per g.), the yield fell to 7% (Found : N, 9·9. $C_{24}H_{21}N_3Se$ requires N, 9·75%). The bright yellow crystals had m. p. 140° (decomp.). The absorption curve had a maximum at 4070 A. and an inflexion at 3550 A. The substance did not sensitise a gelatino-chloride photographic emulsion.

In a second method of preparation, 3-ethyl-2-methylenebenzselenazoline (22·4 g.; 1 mol.), ethyl*iso*formanilide (75 c.c.; 5 mols.) and zinc chloride (41 g.; 3 mols.) were heated together at 150—170° for 2 hours. The washed product was boiled out with methyl alcohol (1000 c.c.), leaving a residue of zinc chloride complex (5·62 g.). The yield of crude base was 10%, falling to 7% on recrystallisation from methyl alcohol. M. p. and mixed m. p. showed its identity with the sample prepared by the first method. A by-product (5·25 g.) which separated from the methyl-alcoholic extract of crude zinc chloride complex was identified as follows as a zinc chloride complex of 3-ethyl-2-aniloethylidenebenzselenazoline. It was treated with 40% sodium hydroxide solution (40 c.c.) and acetone (100 c.c.); on pouring the concentrated acetone extract into water, a base (4·11 g.) resulted, and after recrystallisation from light petroleum (b. p. 80—100°), consisted of a 20% yield (2·83 g.) of what was proved to be 3-ethyl-2-aniloethylidenebenzselenazoline, by comparison with a genuine specimen.

It is noteworthy that we were unable to prepare the dianilo-base by the action of ethyl*iso*formanilide and zinc chloride on the zinc chloride complex of 3-ethyl-2-aniloethylidenebenzselenazoline, which tallies with the fact that it could not be thus prepared from the hydrochloride either, *i.e.*, from 2-β-anilinovinylbenzselenazole ethochloride.

4-Methyl-3-ethyl-2-dianiloisopropylidene-Δ⁴-thiazoline (XIII).—4-Methyl-3-ethyl-2-aniloethylidene-Δ⁴-thiazoline (48·8 g.; 1 mol.), ethyl*iso*formanilide (152 g.; 5 mols.), and zinc chloride (80 g.; 3 mols.) were heated together at 150—170° for 2 hours. The crude zinc chloride complex was washed with acetone, treated with water, and boiled out with methyl alcohol (3200 c.c.) (64·8 g. left). It was then shaken vigorously at room temperature with 40% sodium hydroxide solution (560 c.c.) and acetone (3200 c.c.). The acetone extract was concentrated to small bulk and the base precipitated by addition of ice-water (31·6 g. obtained). On recrystallisation from light petroleum (b. p. 80—100°; 35 c.c. per g.), a 35% yield (23·9 g.) of golden-yellow crystals was obtained (Found : S, 9·05. $C_{21}H_{21}N_3S$ requires S, 9·25%). M. p. 111° (decomp.). The absorption maximum was at 3475 A. The *base* was inert towards a gelatino-chloride photographic emulsion.

3-Methyl-2-dianiloisopropylidenethiazolidine.—3-Methyl-2-aniloethylidenethiazolidine (10·20 g.; 1 mol.), ethyl*iso*formanilide (70 c.c.; 10 mols.), and zinc chloride (19·13 g.; 3 mols.) were heated together at 175—180° for 1½ hours. The warm viscous mass was treated with acetone (150 c.c.). The solid was filtered off, treated with water (300 c.c.), and boiled out four times with methyl alcohol (125 c.c. × 4) (12·85 g. of zinc chloride complex left).

In order to liberate the free base, the zinc chloride complex (8 g.) was ground with acetone (120 c.c.), and the mixture cooled with ice and stirred mechanically. An ice-cold solution of sodium (2 g.) in absolute alcohol (120 c.c.) was run in, and stirring with cooling was applied for 10 minutes; when the sodium ethoxide solution was first added, the liquid became bright yellow. The solid, which apparently consisted of zinc oxide and sodium zincate, was filtered off and washed with acetone (16 c.c.). On pouring the filtrate and washings into ice-cold water (500 c.c.), the *base* was precipitated as a yellow solid, being obtained in 36% yield (3·33 g.). Rapid recrystallisation from methyl alcohol (25 c.c. per g.) gave a 30% yield, but when boiling and mechanical stirring were applied for 5 minutes, decomposition took place, so that the yield was only 4% (Found : S, 9·95. $C_{18}H_{18}N_2S$ requires S, 10·0%). Recrystallisation from light petroleum (b. p. 80—100°) was less precarious and gave an 18% yield. The lemon-yellow crystals had m. p. 127°. The absorption maximum was at 3720 A. The base was photographically inert.

3-Ethyl-2-dianiloisopropylidenethiazolidine.—The zinc chloride complex (66 g.) was prepared similarly from 3-ethyl-2-aniloethylidenethiazolidine (90·6 g.) and was converted (in 20 g. lots) into the free *base*, of which the yield was 33% (43 g.). After recrystallisation from light petroleum (b. p. 80—100°; 120 c.c. per g.), the yield was 22% (Found, after drying in a vacuum at 50° : S, 9·6. $C_{20}H_{21}N_3S$ requires S, 9·55%). The bright yellow crystals had m. p. 104°. The absorption maximum of the broad curve was at 3530 A. The base was photographically inert in a gelatino-chloride emulsion.

1-Ethyl-4-dianiloisopropylidene-1 : 4-dihydroquinoline (VIII).—1-Ethyl-4-methylene-1 : 4-dihydroquinoline (10·44 g.; 1 mol.) was treated with ethyl*iso*formanilide (90·5 c.c.; 10 mols.) and zinc chloride powder (25 g.; 3 mols.) and the mixture was heated in an oil-bath and stirred by hand until the temperature reached 80° and the large lumps had been broken up. Mechanical stirring was then applied and the mixture was heated at 175—185° for 1¼ hours. Whilst still warm, the reaction mixture was treated with acetone (150 c.c.), whereupon hardening occurred. After intermittent heating, the dark syrupy liquid was poured off and the hard residue heated with another equal amount of acetone, and finally with yet another, which left no residue. All the dark mixtures were filtered after cooling and the residual solid was further washed with acetone, and with water (600 c.c.). The solid was boiled out thrice with methyl alcohol (400 c.c. × 3). The first filtrate was almost black, the second dark brown, the third amber, and the residual solid (12·74 g.) a clean, bright orange.

In order to obtain the base, the zinc chloride complex (2 g.) was ground with acetone (30 c.c.), and the suspension cooled with ice and treated with an ice-cold solution of sodium (0·45 g.) in absolute alcohol (30 c.c.). The solid was crushed until orange streaks were no longer visible : the liquid became dark yellow. The grey residue was filtered off and washed with a cooled alcohol–acetone mixture : the filtrates were poured into ice-cold water (60 c.c.). Before the bright yellow solid could be filtered off it had become brown. It was washed with ice-cold water and dried in the air and finally in a vacuum desiccator. The yield of base was 34% (1·24 g.). 1 G. was twice extracted with hot light petroleum (b. p. 40—60°; 20 c.c. × 2), each extract being filtered into a tube cooled with ice. The yield of recrystallised product was only 3% (Found, after drying in a vacuum desiccator : N, 11·0. $C_{24}H_{23}N_2$

requires N, 11·15%). When heated, the light brown powder began to shrink at 90°; decomposition was gradual and the substance was quite black by 154° but without any definite m. p. The absorption maximum was at 4785 A., with another maximum at 4020. The *base* sensitised a gelatino-chloride photographic emulsion weakly up to 5400 A., with the maximum at 4950.

1-*Ethyl*-2-*dianiloisopropylidene*-1 : 2-*dihydroquinoline*.—1-Ethyl-2-methylene-1 : 2-dihydroquinoline (10·14 g.) was heated with ethyl*iso*formanilide and zinc chloride as in the previous preparation. The warm product was treated with acetone (120 c.c.) and left to stand, with occasional warming. The suspension was poured off from the hard residue, which was similarly treated with a second portion of acetone (120 c.c.) and later with a third (120 c.c.). After cooling, the extracts were filtered, giving a black, treacly filtrate. The residual product was washed with acetone, ground with water (400 c.c.), and thrice boiled out with methyl alcohol (750 c.c. × 3). The residue of zinc chloride complex was a dull orange (7·31 g. obtained).

Its conversion into *base* was carried out as in the preceding preparation. The yield of washed, dried base was 7% (0·82 g. from two 2 g. lots of complex). It was a dirty yellow when first precipitated but finally a dark green. On recrystallising as quickly as possible from light petroleum (b. p. 80—100°; 60 c.c. per g.), the yield dropped to 1% (Found, after drying in a vacuum desiccator: N, 10·85. $C_{24}H_{22}N_2$ requires N, 11·15%). The light brown powder had no definite m. p.; shrinking began at about 95° and considerable decomposition had occurred by 105°. The broad absorption curve had its maximum at 4100 A. On a gelatino-chloride emulsion the base conferred traces of sensitivity up to 5200 A.

3-*Ethyl*-2-*dianiloisopropylidenebenzoxazoline*.—3-Ethyl-2-aniloethylidenebenzoxazoline (106 g.; 1 mol.), ethyl*iso*formanilide (300 c.c.; 5 mols.) and zinc chloride (168 g.; 3 mols.) were heated together at 150—160° for 1 hour. The reaction mixture was heated with acetone, and the solid boiled out with methyl alcohol (1600 c.c.). The resultant zinc chloride complex (45 g.) was warmed and shaken with 20% sodium hydroxide solution (7·5 c.c. per g.) and acetone (65 c.c. per g.). After concentration, the acetone extract was precipitated with aqueous ammonium chloride solution, and the crude base recrystallised from methyl alcohol (100 c.c. per g.) (18 g. obtained). As a sample left some ash on heating, the base was purified by suspending it in spirit (20 c.c. per g.) and acidifying with concentrated hydrochloric acid (4 c.c. per g.). The filtered solution was treated with ammonia and the precipitated *base* was obtained in 6% yield (8·6 g.). On recrystallisation from methyl alcohol (700 c.c.), the yield dropped to 4% (5·3 g.) and on a second recrystallisation (from 450 c.c.) to 3% (Found: N, 11·6. $C_{24}H_{21}ON_3$ requires N, 11·45%). The bright yellow crystals had m. p. 210° (decomp.). The absorption maximum was at 3755 A. The compound was photographically inert.

[*Bis*-2-(3-*ethylbenzthiazole*)][*αβ'-dimethin*-2'-(3'-*ethylbenzthiazole*)]*trimethincyanine Di-iodide* (XII).—3-Ethyl-2-dianilo*iso*propylidenebenzthiazoline (XI) (0·19 g.; 1 mol.) was ground with 2-methylbenzthiazole ethiodide (0·31 g.; 2 mols.) and the mixture heated with pyridine (2 c.c.) at 130—140° for 5 minutes. A blue colour rapidly developed and solid crystallised. It was filtered off when cold and washed with pyridine and with ether, being obtained in 90% yield (0·36 g.). After recrystallisation from methyl alcohol (100 c.c. per g.) it was obtained in 74% yield (0·28 g.) (Found: I, 31·55. $C_{33}H_{31}N_3I_2S_3$ requires I, 31·45%). The dark green crystals had m. p. 243° (decomp.). The absorption maximum was at 6015 A. with an inflexion to the curve at 5550. The *dye* caused weak photographic sensitisation, extending to 7000, with its maximum at 6450 A.

In a preparation in which the pyridine was replaced by anhydrous sodium acetate (0·33 g.; 8 mols.) and acetic anhydride (2 c.c.), the yield of crude product, after washing with acetic anhydride, ether, and water, was 65%, and after recrystallisation from methyl alcohol it was 55%.

Ogata (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 497; cf. *idem*, *Proc. Imp. Acad. Tokyo*, 1933, **9**, 602) heated together 2-methylbenzthiazole ethiodide, orthoformic ester, and succinic acid at 170°, and claimed a 15% yield of thiacarbocyanine and a 1% yield of more soluble neocyanine, with no indication that a troublesome purification is necessary. In repeating the preparation, our best result was obtained by heating together 2-methylbenzthiazole etho-*p*-toluenesulphonate (3 g.; 3 mols.), succinic acid (2·72 g.; 8 mols.), and ethyl orthoformate (3 c.c.; 3·2 mols.) at 180—190° for 10 minutes. After cooling, the liquid was poured off, and the residual tar washed with absolute ether (25 c.c.). It was then heated with a solution of crystalline sodium carbonate (6·6 g.; 8 mols.) in water (10 c.c.), so as to remove any succinic acid. To convert the dyes into iodides, potassium iodide (3 g.) was added and the green solid was filtered off. In addition to a dye giving a pink and one giving a blue solution, other matter was present. After two washings with water (10 c.c. × 2), the residue (1·18 g.) was thrice boiled out with methyl alcohol (10 c.c. × 3). The blue dyes from the first two fractions were put together (0·33 + 0·13 g.), but the bluish-pink dye (0·10 g.) from the third was rejected. The residue was recrystallised from absolute alcohol (50 c.c.) and gave the pink thiacarbocyanine (0·20 g.). On precipitating the combined methyl-alcoholic filtrates with absolute ether (150 c.c.), a further yield of the blue dye was obtained (0·06 g., making the total 0·52 g.). The dye giving a blue solution was twice boiled out with absolute alcohol (50 c.c. per g. × 2), and was then recrystallised from methyl alcohol (50 c.c. per g.), in which the neocyanine was considerably more soluble than in absolute alcohol. The final yield of purified thiacarbocyanine was 17% (0·15 g.) and of purified *neocyanine* 9% (0·09 g.) (Found: I, 31·9. $C_{33}H_{31}N_3I_2S_3$ requires I, 31·45%). Ogata correlated his nitrogen determination with the formula $C_{31}H_{31}N_3I_2S_3$ and gave m. p. 256° (decomp.). The present specimen was found to have the same m. p., mixed m. p., and absorption as the synthetic one.

[*Bis*-2-(3-*ethylbenzthiazole*)][*αβ'-dimethin*-2'-(3'-*ethylbenzthiazole*)]*trimethincyanine Dichloride*.—The preceding di-iodide (0·88 g.) was converted into the *dichloride* by boiling its solution in spirit (176 c.c.) with freshly precipitated silver chloride and taking the filtered solution down to dryness. The dichloride (0·52 g.; 76% yield) was given two recrystallisations from ethyl alcohol (3 c.c. per g.) and ethyl acetate (18 c.c. per g.) and thus obtained in 49% yield (Found: Cl, 10·6; S, 14·4. $C_{33}H_{31}N_3Cl_4S_3,C_2H_5OH$ requires Cl, 10·4; S, 14·35%). Its green crystals melted at about 200° (decomp.). It was insoluble in anhydrous ether or in ethyl acetate but readily soluble in methyl or ethyl alcohol and in water.

[*Bis*-2-(3-*ethyl*-6 : 7-*benzbenzthiazole*)][*αβ'-dimethin*-2'-(3'-*ethyl*-6' : 7'-*benzbenzthiazole*)]*trimethincyanine Di-iodide*.—3-Ethyl-2-dianilo*iso*propylidene-6 : 7-benzbenzthiazoline (0·87 g.; 1 mol.) and 2-methyl-6 : 7-

benzbenzthiazole ethiodide (1·42 g.; 2 mols.) were ground together, treated with pyridine (16 c.c.), and heated with mechanical stirring at 130—140° for 10 minutes. The washed solid was recrystallised from methyl alcohol (600 c.c.) and gave a 56% yield (1·07 g.). A second recrystallisation from spirit (630 c.c. per g.) gave a 36% yield. Filtration of the recrystallised *dye* was extraordinarily slow (Found : I, 26·2. $C_{44}H_{37}N_3I_2S_3$ requires I, 26·5%). The dark bronze substance had m. p. 216° (decomp.). The absorption maximum was at 6350 A. with an inflexion to the curve at 5900 A. The dye did not sensitise but caused some depression of the normal sensitivity of the plate.

[*Bis*-2-(5-*chloro*-3-*ethylbenzthiazole*)][$\alpha\beta'$-*dimethin*-2′-(5′-*chloro*-3′-*ethylbenzthiazole*)]*trimethincyanine Di-iodide*.—5-Chloro-3-ethyl-2-dianilo*iso*propylidenebenzthiazoline (1·56 g.; 1 mol.), 5-chloro-2-methylbenzthiazole ethiodide (2·55 g.; 2 mols.), anhydrous sodium acetate (1·23 g.; 4 mols.), and acetic anhydride (10 c.c.) were heated together at 150° for 10 minutes. The washed *dye* (2·93 g.; 86% yield) was recrystallised from methyl alcohol (320 c.c. per g.), after which the yield was 51% (Found : 3 Cl + 2I, 39·35. $C_{33}H_{28}N_2Cl_3I_2S_2$ requires 3Cl + 2I, 39·55%). The green crystals had m. p. 240° (decomp.). The absorption maximum was at 6105 A. with an inflexion to the curve at 5700 A. The compound did not sensitise and strongly depressed the blue sensitivity of a photographic emulsion. A pure product was not obtained in earlier experiments where the condensing agent was pyridine.

[*Bis*-2-(3-*ethylbenzselenazole*)][$\alpha\beta'$-*dimethin*-2′-(3′-*ethylbenzselenazole*)]*trimethincyanine Di-iodide* (XV).—3-Ethyl-2-dianilo*iso*propylidenebenzselenazoline (0·66 g.; 1 mol.), 2-methylbenzselenazole ethiodide (1·06 g.; 2 mols.), and pyridine (6 c.c.) were heated and stirred together at 135—140° for 5 minutes. On recrystallising the washed *dye* (0·93 g. obtained; 65% yield) from methyl alcohol (195 c.c. per g.), the yield was 56% (0·80 g.) (Found : I, 26·85. $C_{33}H_{31}N_3I_2Se_2$ requires I, 26·75%). The dull green crystals had m. p. 226° (decomp.). The absorption maximum was at 6200 A., with an inflexion to the curve at about 5740 A. The compound had a strong desensitising effect on a photographic plate.

[*Bis*-2-(4-*methyl*-3-*ethylthiazole*)][$\alpha\beta'$-*dimethin*-2′-(4′-*methyl*-3′-*ethylthiazole*)]*trimethincyanine Di-iodide* (XIV).—4-Methyl-3-ethyl-2-dianilo*iso*propylidene-Δ^4-thiazoline (XIII) (0·69 g.; 1 mol.), 2 : 4-dimethylthiazole etho-*p*-toluenesulphonate (1·25 g.; 2 mols.), and pyridine (5 c.c.) were heated together at 130° for 40 minutes. The pyridine was removed under reduced pressure, and the residue dissolved in hot spirit and poured into a hot aqueous solution of potassium iodide (2·2 g.; 8 mols.). The dye (1·04 g.; 74% yield) was recrystallised from absolute alcohol (20 c.c.) and thus obtained in 59% yield (0·82 g.) as dark blue crystals (Found : I, 36·25. Calc. for $C_{23}H_{21}N_3I_2S_3$: I, 36·3%); it had m. p. 206° (decomp.), which was also the m. p. of the mixture of this synthetic specimen with that of the one prepared by the empirical method given below. The substance had a narrow absorption curve with its maximum at 5875 A. It sensitised to 7100 A., the maximum lying at 6300. In these respects it was identical with the sample prepared by the following method.

By the empirical method, 2 : 4-dimethylthiazole etho-*p*-toluenesulphonate (31 g.), ethyl orthoformate, and pyridine were boiled together for 5 hours (Kodak Ltd. and Brooker, B.P. 408,273/1931). The product (6·23 g.) obtained by concentration in a vacuum, followed by precipitation with potassium iodide, was boiled out four times with methyl alcohol (15 c.c. × 3, 25 c.c.). The fraction which crystallised from the first two extracts was combined with a second crop which resulted on concentration of the first three filtrates (total 5·2 g.). This was given a second fractional crystallisation from absolute alcohol (20 c.c., 25 c.c.) and methyl alcohol (15 c.c.) but this time there was no residue and the neocyanine crystallised in 18% yield (3·97 g.) (Found : I, 36·2%). In the first fractional crystallisation, the less soluble residue (0·46 g.) was combined with the dye which crystallised from the last two extracts (0·47 g.) and was recrystallised from methyl alcohol (100 c.c.), being obtained in 3% yield (0·6 g.) (Found : I, 30·3. Calc. for $C_{15}H_{21}N_2IS_2$: I, 30·2%). This is bis-2-(4-methyl-3-ethylthiazole)trimethincyanine iodide, identical with that prepared by Fisher and Hamer (*J.*, 1930, 2502).

[*Bis*-2-(3-*methyl*-Δ^2-*thiazoline*)][$\alpha\beta'$-*dimethin*-2′-(3′-*methyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Di-iodide* (XVI; R = Me, X = I). 3-Methyl-2-dianilo*iso*propylidenethiazolidine (0·64 g.; 1 mol.), 2-methyl-Δ^2-thiazoline methiodide (1·07 g.; 2·2 mols.), and pyridine (8 c.c.) were heated together at 130—140° for 2 minutes. The washed *dye* (0·83 g.; 67% yield) was recrystallised from methyl alcohol (25 c.c.). The yield was 53% (0·65 g.) and after a second recrystallisation from methyl alcohol (40 c.c. per g.) it was 42% (Found : I, 40·95. $C_{17}H_{25}N_3I_2S_3$ requires I, 40·85%). When the purplish-red crystals were heated they began to shrink at about 115° and had largely melted and decomposed by 125° but there was no definite m. p. The absorption maximum was at 5065 A. The dye sensitised a gelatino-bromide photographic emulsion up to 5900 A.

[*Bis*-2-(3-*ethyl*-Δ^2-*thiazoline*)][$\alpha\beta'$-*dimethin*-2′-(3′-*ethyl*-$\Delta^{2'}$-*thiazoline*)]*trimethincyanine Diperchlorate* (XVI; R = Et, X = ClO_4).—3-Ethyl-2-dianilo*iso*propylidenethiazolidine (1·02 g.; 1 mol.), 2-methyl-Δ^2-thiazoline ethiodide, and pyridine were heated together at 130—140° for 5 minutes. The gum, precipitated by absolute ether, was dissolved in hot spirit (30 c.c.) and treated with a hot solution of sodium perchlorate (1·68 g.; 4 mols.) in water (30 c.c.). The crude *perchlorate* (1·59 g.) was boiled out with and recrystallised from methyl alcohol (15 c.c., 225 c.c.), the product being obtained in 51% yield (0·93 g.) (Found : Cl, 11·7. $C_{20}H_{21}O_8N_2Cl_3S_2$ requires Cl, 11·65%). The brick-red crystals had m. p. 230° (decomp.). The absorption maximum was at 5060 A. In a gelatino-bromide photographic emulsion the compound produced extra-sensitivity up to 5700 A.

[*Bis*-4-(1-*ethylquinoline*)][$\alpha\beta'$-*dimethin*-4′-(1′-*ethylquinoline*)]*trimethincyanine Di-iodide*.—Crude 1-ethyl-4-dianilo*iso*propylidene-1 : 4-dihydroquinoline (VIII) (0·75 g.; 1 mol.), lepidine ethiodide (1·20 g.; 2 mols.), and anhydrous sodium acetate (1·31 g.; 8 mols.) were ground together, treated with acetic anhydride (8 c.c.), and heated at 135—140° for 10 minutes. Brassy crystals of dye began to separate when the temperature reached 110°. The solid was filtered off, washed with acetic anhydride and with ether, ground with water (10 c.c.), washed with methyl alcohol, and boiled out with it three times (20 c.c. × 3). The first fraction was rejected but the dye which crystallised from the second and third (0·01 g.) was put with the undissolved residue (0·41 g.) making a 27% yield (0·42 g.). On recrystallisation from methyl alcohol (1000 c.c. per g.) the yield was 20% (0·32 g.) (Found : I, 32·3. Calc. for $C_{38}H_{37}N_3I_2$: I, 32·15%). When samples of the original neocyanine ethiodide (Hamer, *J.*, 1928, 1472), of the present synthetic dye, and of their mixture were heated, all melted simultaneously at 280° (decomp.).

We failed to isolate the dye when heating with pyridine took the place of heating with sodium acetate and acetic anhydride, but in another experiment 1-ethyl-4-dianilo*iso*propylidene-1 : 4-dihydroquinoline (0·19 g.; 1 mol.) and excess of lepidine ethiodide (0·45 g.; 3 mols.) were ground together, treated with ice-cold pyridine (2 c.c.), and left in the cold for six days, with occasional stirring. The crystals were filtered off and well washed; the residue (0·12 g.) was twice boiled out with methyl alcohol (15 c.c., 25 c.c.), and the product which crystallised (0·01 g.) added to what remained (0·02 g.), making up a 7% yield. After recrystallisation from methyl alcohol (30 c.c.), the yield of the characteristic brassy crystals was 2% (0·01 g.).

Bis-2-(5-*chloro*-3-*ethylbenzthiazole*)*pentamethincyanine Iodide.*—5-Chloro-2-methylbenzthiazole ethiodide (1·97 g.; 2 mols.) and β-anilinoacraldehyde anil hydrochloride (0·75 g.; 1 mol.) in boiling absolute alcohol (20 c.c.) were treated with a solution of sodium (0·14 g.; 2 atoms) in absolute alcohol (5 c.c.). The mixture was boiled and stirred for 3 minutes, during which time the solids dissolved and a green dye separated. After three recrystallisations of the washed *dye* (1·35 g.; 80% yield) from methyl alcohol (2600 c.c., 3900 c.c., and 5000 c.c. per g.) the yield was 38% (Found: 2Cl + I, 33·55. $C_{23}H_{21}N_2Cl_2IS_2$ requires 2Cl + I, 33·7%). The bluish-green crystals had m. p. 298° (decomp.). The absorption maximum was at 6560 A. The dye sensitised a gelatino-bromide photographic emulsion from 6500—7400 A., with a maximum at 7000 A. This preparation was carried out by Dr. V. P. Pittman, whom we thank.

Bis-2-(4-*methyl*-3-*ethylthiazole*)*pentamethincyanine Iodide.*—2 : 4-Dimethylthiazole etho-*p*-toluenesulphonate (12·52 g.; 2 mols.), β-ethoxyacraldehyde diethyl acetal (3·84 g.; 1·1 mols.), and triethylamine (5·6 c.c.; 2 mols.) in pyridine (40 c.c.) were boiled and stired together for 7 minutes. Ether precipitated a sticky solid which was dissolved in hot spirit and treated with a solution of potassium iodide (13 g.; 4 mols.) in hot water. The crude *dye* (2·3 g.) was boiled out with and recrystallised from absolute ethyl alcohol (15 c.c., 100 c.c.), being obtained in 21% yield (1·92 g.) (Found: I, 28·3. $C_{17}H_{23}N_2IS_2$ requires I, 28·45%). The steely bluish-green crystals had m. p. 214° (decomp.). The absorption curve had its maximum at 6370 A. and an inflexion at 6050 A. It sensitised from 6500—6900 A. with the maximum at 6800 A.

Bis-2-(3-*ethyl*-Δ^2-*thiazoline*)*pentamethincyanine Iodide.*—A mixture of 2-methyl-Δ^2-thiazoline ethiodide (3·98 g.; 2 mols.), β-anilinoacraldehyde anil hydrochloride (2 g.; 1 mol.), anhydrous potassium carbonate (5·36 g.; 5 mols.; 180-mesh), and ethyl alcohol (10 c.c.) was boiled for 4 minutes. The washed solid (1·71 g.) was recrystallised from methyl alcohol (10 c.c.) and obtained in 27% yield (0·88 g.). After a second recrystallisation from methyl alcohol (10 c.c.), the yield was 24% (0·77 g.) (Found: I, 30·2. $C_{15}H_{23}N_2IS_2$ requires I, 30·05%). The steely crystals had m. p. 231° (decomp.). The absorption maximum was at 5450 A. The *dye* sensitised a gelatino-bromide photographic emulsion, the maximum lying at 5700 A.

We are indebted to Miss M. D. Gauntlett for the absorption measurements and to Drs. B. H. Carroll and E. B. Knott for the sensitising tests.

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272. *The Galactomannan of the Lucerne Seed.*

By E. L. HIRST, J. K. N. JONES, and WINIFRED O. WALDER.

The mucilagenous polysaccharide in the lucerne seed has been shown to consist of a galactomannan containing galactose and mannose in the approximate ratio of 2 to 1. Hydrolysis of the methylated polysaccharide gave a mixture of sugars among which 2 : 3 : 4 : 6-tetramethyl *d*-galactose, 2 : 4 : 6-trimethyl *d*-galactose, and 3 : 4-dimethyl *d*-mannose were detected. The general type of structure present in the polysaccharides is discussed on the basis of this evidence.

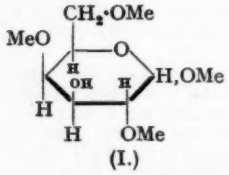
POLYSACCHARIDES other than cellulose are of common occurrence in the cell walls of many plants. They are, in general, insoluble in water but form solutions in dilute sodium hydroxide from which they may be precipitated by the addition of alcohol. Investigation of the hemicelluloses from cell walls, with special reference to the endosperm of ungerminated seeds, has revealed the presence of a number of different polysaccharides. Amongst these are the galactomannans which occur in the endosperm of the seeds of *Phœnix dactylifera*, *Elæis guinensis*, *Cocos nucifera*, *Coffea arabia* (Schulze, Steiger, and Maxwell, *Z. physiol. Chem.*, 1890, **14**, 227), and lucerne seed (May and Schulze, *Z. Biol.*, 1936, **97**, 201; Wise and Appling, *Ind. Eng. Chem. Anal.*, 1944, **16**, 28). Galactomannans have also been shown to occur in the seeds of the Fenugreek (Daoud, *Biochem. J.*, 1932, **26**, 255) and in the Carob bean (Spada, *Atte. Soc., Nat. Mat. Modena*, 1939, **70**, 20). It appears that these polysaccharides may function as reserve material in the seed and are utilised by the seed during germination (Schulze, *Landw. Jahrb.*, 1894, **23**, 1; *Ber. deut. bot. Ges.*, 1896, **14**, 66). In view of these observations and since some of the galactomannans have physical properties closely resembling those of the mucilages it was considered of interest to determine the mode of linkage of the sugars in the polysaccharide molecule.

The polysaccharide was isolated from lucerne seeds by the procedure given by Schulze

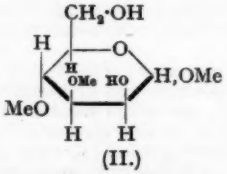
(*loc. cit.*). It was a white powder which did not reduce Fehling's solution and gave aqueous solutions of comparatively high viscosity. It underwent hydrolysis with boiling N-sulphuric acid at a rate indicating the presence of pyranose sugar residues in the molecule, and a quantitative determination of the sugars proved that *d*-mannose and *d*-galactose were present in the approximate ratio of 1 to 2. No other sugar could be detected.

The fully methylated galactomannan was obtained by reaction with sodium hydroxide and methyl sulphate followed by further treatment of the thallium hydroxide complex of the partially methylated derivative with methyl iodide.

The methylated polysaccharide, which was essentially homogeneous, was resistant to methyl-alcoholic hydrogen chloride. Hydrolysis was effected by use of a mixture of hydrochloric acid and glacial acetic acid which has been shown by Bell (*Biochem. J.*, 1935, **29**, 2031) to be efficacious in the hydrolysis of resistant polysaccharides. The products were isolated as the methylglycosides, and on distillation fractions containing the following sugars were obtained: (1) 2 : 3 : 4 : 6-tetramethyl methyl-*d*-galactoside, identified after hydrolysis and formation of the characteristic crystalline anilide of tetramethyl *d*-galactose; (2) 2 : 4 : 6-trimethyl *d*-methylgalactoside (I), identified after hydrolysis as the crystalline sugar and as its crystalline anilide; and (3) 3 : 4-dimethyl *d*-methylmannoside (II), isolated after hydrolysis and oxidation as the crystalline 3 : 4-dimethyl *d*-mannonamide (III). Intermediate fractions were also obtained.



(I.)



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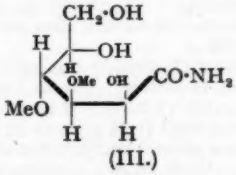

(III.)

The isolation of these sugars proves that the galactomannan is not a mixture of a galactan and a mannan. This follows since a polysaccharide built of solely glycosidically linked mannose residues, some of which are present in a form having three points of linkage with other mannose residues, must possess a corresponding number of residues connected to others only by one linkage. The experimental results show clearly that no such mannose end groups are present, and it follows that the mannose residues must be present in a structure containing galactose also. The sugar residues isolated are all in the pyranose form and are substituted on C_4 by a methoxyl group. The isolation of a large amount of 2 : 3 : 4 : 6-tetramethyl *d*-galactose (*ca.* 30%) proves that the polysaccharide is of the branched-chain type and that half the galactose residues are terminal groupings. Unfortunately, the exact ratios of 2 : 4 : 6-trimethyl *d*-galactose and 3 : 4-dimethyl *d*-mannose could not be accurately determined in these experiments since some of the intermediate fractions which had not been fully examined were lost by enemy action. Nevertheless, an inspection of the methoxyl figures indicates that the relative molecular proportions of 2 : 3 : 4 : 6-tetramethyl methyl-*d*-galactoside, trimethyl methylhexoside, and dimethyl methylhexoside are 1 : 1 : 1. At least one-third of the dimethyl methylhexoside is known to be 3 : 4-dimethyl methylmannoside, and at least one-third of the trimethyl methylhexoside is 2 : 4 : 6-trimethyl methylgalactoside. A further investigation will be necessary in order to determine whether or not other sugars are present amongst the products of hydrolysis. In the meantime it is clear that half the galactose residues are attached in the form Gal . . . and therefore are end groups. Another set of galactose residues is present in the form . . 3Gal . ., linked through positions 1 and 3, and at least one-third of the mannose residues occur as . . $\overset{6}{\underset{2}{\text{Man}}}$ . ., linked through positions 1, 2, and 6.

It will be observed that the 1 : 3 galactose linkage so common in polysaccharides containing galactose, and the 1 : 6 and 1 : 2 mannose linkages occurring in damson gum, cherry gum (Hirst, *J.*, 1942, 70), and yeast mannan (Haworth, Hirst, and Isherwood, *J.*, 1937, 784; Haworth, Hart, and Peat, *J.*, 1941, 833), also occur in this galactomannan.

Experimental.

(All temperatures recorded for distillations are bath temperatures).

Lucerne seeds (500 g.) were finely ground and heated at 100° for 8 hours, with continuous stirring, with 10% potassium hydroxide solution (4 l.) until a jelly-like mass was formed and no more ammonia was evolved. The alkaline solution was then poured with stirring into alcohol (8 l.), and the dark solid which separated was washed with alcohol by decantation and filtered off. The precipitate was

purified by reprecipitation from water with alcohol. Insoluble cell-wall material was then removed by heating the solid with potassium hydroxide solution (4 l.) for 3 hours, cooling, and centrifuging. The insoluble residues were extracted repeatedly until the extracts gave no precipitate on addition of alcohol. The combined extracts were then poured into alcohol (4 vols.) and the precipitate was filtered off and further purified by reprecipitation from acidified aqueous solution (hydrochloric acid) with alcohol.

Traces of starch were removed from the polysaccharide by the action of "taka-diastase" (0·05%) at 37° for 12 hours. Further purification was achieved by precipitation of the copper complex by the addition of copper sulphate solution to a hot alkaline solution of the crude polysaccharide until no further material was precipitated. The copper complex was washed well with hot water and filtered off. The complex was decomposed by grinding it with alcohol containing hydrochloric acid, and the regenerated polysaccharide was ground and washed with alcohol until free from copper and chloride ions. Finally, the product was purified by dissolving it in water and precipitating it from the aqueous solution with alcohol, and dried in vacuum. Yield, 10 g. of a white powder, which dissolved in water to form viscous non-reducing solutions; $[\alpha]_D^{20°}$ + 89° (Found: furfuraldehyde, 2; uronic acid, nil; N, nil; mannose, determined as the phenylhydrazone after hydrolysis with N-sulphuric acid at 95° for 2½ hours, 29·6; galactose, determined as the phenylmethylhydrazone after the same treatment, 58%; equiv. by titration with 0·1N-sodium hydroxide, 4540).

Methylation of the Polysaccharide.—The pure polysaccharide (25 g.) was dissolved in water (300 c.c.) and 30% sodium hydroxide (400 c.c.), and methylated with methyl sulphate (200 c.c.) added in portions (30 c.c.) at 20 minute intervals. The methylation was carried out in an atmosphere of nitrogen and with the usual precautions. After 24 hours the cooled solution was partly neutralised with dilute sulphuric acid and concentrated under reduced pressure. The residue was then re-methylated using the conditions described above. Two repetitions of this process gave a crude methylated product (isolated in the usual manner) which was freed from sodium sulphate and other salts by dialysis. Yield, 15·5 g. (Found: OMe, 34·0%). To complete the methylation the product was dissolved in ethyl alcohol (100 c.c.) and benzene (100 c.c.), and a solution of thallium ethoxide (1·7N, 100 c.c.) in benzene added. Solvent was removed under reduced pressure and the residual solid finely powdered (150 mesh) and boiled under reflux with methyl iodide (150 c.c.) for 30 hours. Excess of methyl iodide was boiled off and the residual solid extracted exhaustively with acetone. Concentration of the extracts gave a residue of partially methylated galactomannan (15 g.) (Found: OMe, 36·2%). This methylation process with thallium ethoxide and methyl iodide was repeated (see above), and the isolated product (13 g.) methylated with silver oxide (10 g.) and methyl iodide (30 c.c.). Repetition of this process gave a product (13 g.) (Found: OMe, 43·5%) isolated in the usual manner.

Fractionation of the Methylated Polysaccharide.—The methylated polysaccharide (10·1 g.) was fractionally precipitated from chloroform by the addition of light petroleum (b. p. 40—60°) giving: Fraction I (2·1 g.), a white solid, $[\alpha]_D^{20°}$ + 72° (*c*, 1·0 in chloroform) (Found: OMe, 43·4%; furfuraldehyde, nil); Fraction II (6·0 g.), a white solid, $[\alpha]_D^{20°}$ + 71° (*c*, 1·1 in chloroform) (Found: OMe, 43·2%; furfuraldehyde, nil); Fraction III (0·9 g.), a white solid, $[\alpha]_D^{20°}$ + 69° (*c*, 0·9 in chloroform) (Found: OMe, 44·1%; furfuraldehyde, nil); Fraction IV (1·0 g.), a sticky solid.

Hydrolysis of the Methylated Polysaccharide.—Hydrolysis of the methylated material was difficult as the product was relatively stable to boiling methyl-alcoholic hydrogen chloride and to hot N-hydrochloric acid. The following procedure was eventually adopted as the most satisfactory technique. The methylated polysaccharide (7·3 g., Fractions I and II) was dissolved in a mixture of glacial acetic acid (50 c.c.), water (25 c.c.), and concentrated hydrochloric acid (25 c.c.), and heated at 100° for 6 hours. Changes in optical rotation were not observable, but preliminary experiments had shown that the hydrolysis was complete at the end of this time. Barium carbonate was added to the cooled solution until a test portion of the solution gave a grey and not a blue colour to Congo-red paper. The solution was then filtered and evaporated to dryness under reduced pressure. The solid residue was then extracted with chloroform, and the extracts were concentrated and boiled with methyl-alcoholic hydrogen chloride (3% w/v) for 12 hours. The cooled solution was then neutralised with silver carbonate and filtered, and the filtrate was concentrated under reduced pressure at 40° to a syrup (6·4 g.) which was fractionally distilled in a vacuum giving: Fraction i (0·86 g.), b. p. 90°/0·001 mm., $n_D^{19°}$ 1·4539 (Found: OMe, 59·5%); Fraction ii (0·72 g.), b. p. 108°/0·001 mm., $n_D^{19°}$ 1·4522 (Found: OMe, 61·9%); Fraction iii (0·53 g.), b. p. 110°/0·001 mm., $n_D^{19°}$ 1·4542 (Found: OMe, 60·0%); Fraction iv (0·57 g.) b. p. 120°/0·01 mm., $n_D^{20°}$ 1·4560 (Found: OMe, 53·8%); Fraction v (1·40 g.), b. p. 130°/0·001 mm., $n_D^{20°}$ 1·4601 (Found: OMe, 48·8%); Fraction vi (1·32 g.), b. p. 160/0·001 mm., $n_D^{20°}$ 1·4680 (Found: OMe, 41·8%); Fraction vii (0·57 g.), b. p. 170°/0·01 mm., $n_D^{20°}$ 1·4780 (Found: OMe, 41·9%); residue, 0·43 g.

Hydrolysis of the Fractions.—The first three fractions having very similar methoxyl values were combined (2·1 g.) and hydrolysed by heating with 2N-hydrochloric acid at 95° for 3 hours; $[\alpha]_D^{20°}$ (initial value not observable), + 71° (2 hours); + 105° (3 hours, constant value). The solution was cooled, neutralised with barium carbonate, and filtered, the filtrate concentrated under reduced pressure, and the residue exhaustively extracted with chloroform. Concentration of the extracts gave a syrup (1·9 g.) which was at least 94% 2 : 3 : 4 : 6-tetramethyl *d*-galactose; $[\alpha]_D^{20°}$ + 109° (in water) (Found: OMe, 52·2. Calc. for $C_{10}H_{20}O_6$: OMe, 51·8%). The sugar (0·32 g.), on being heated under reflux with aniline (0·1 c.c.) dissolved in alcohol (3 c.c.) for 2½ hours, gave 2 : 3 : 4 : 6-tetramethyl *d*-galactose anilide (0·34 g.), m. p. 189°, not depressed on admixture with an authentic sample. Fraction iv (0·56 g.) was hydrolysed by boiling with 2N-hydrochloric acid (25 c.c.) for 3 hours; $[\alpha]_D^{20°}$ + 56° (2 hours); + 70° (3 hours, constant value). The sugar (0·5 g.) was isolated as described above; $[\alpha]_D^{20°}$ + 70° (*c*, 1·0 in water) (Found: OMe, 40·0. Calc. for $C_9H_{18}O_6$: OMe, 41·8%). On standing, the syrup partly crystallised. The crystals were separated by trituration with ether and had m. p. 105°, not depressed on admixture with an authentic specimen of 2 : 4 : 6-trimethyl *d*-galactose. The syrup (0·4 g.) on boiling with aniline (0·3 g.) in ethyl alcohol (2 c.c.) for 2½ hours gave the anilide of 2 : 4 : 6-trimethyl *d*-galactose (0·5 g.), m. p. 179°, not depressed on admixture with an authentic specimen. At the most only traces of 2 : 3 : 6-trimethyl *d*-galactose could be present in the syrup, as on standing with cold 5% methyl-alcoholic hydrogen chloride no downward change of rotation was observable; $[\alpha]_D^{20°}$ + 41° (initial

value); + 49° (3 hours); + 58° (6 hours). Fraction vii (0·57 g.) was hydrolysed with boiling 2N-hydrochloric acid; $[\alpha]_D^{20°}$ + 31° (initial value); 0° (3 hours, constant value). The solution was cooled and neutralised with barium carbonate, and the filtrate was evaporated to dryness. The syrup (0·5 g.), isolated in the usual manner, did not crystallise. The absence of any derivative of mannose or galactose with a hydroxyl group on C_4 was indicated by the fact that the syrup (0·03 g.) in methyl-alcoholic hydrogen chloride (5 c.c.; 5%) showed no change of rotation (+ 10°) in 7 days. The syrup (0·2 g.) was oxidised with bromine water at 45° until non-reducing (7 hours). The cooled solution was neutralised with silver carbonate and filtered, and silver ions were removed with hydrogen sulphide. The filtered solution was concentrated to a syrup (0·15 g.) which did not crystallise. Accordingly, the material was dissolved in liquid ammonia and excess of ammonia allowed to evaporate. The residue crystallised, and by trituration with acetone 3 : 4-dimethyl *d*-mannonamide, m. p. 139°, not depressed on admixture with an authentic specimen, was isolated. The amide gave a strong positive test for an α-hydroxy-amide by the method of Weerman.

A complete examination of Fractions v and vi was not possible since these fractions were lost by enemy action. They obviously contained some 2 : 4 : 6-trimethyl *d*-galactose and 3 : 4-dimethyl *d*-mannose, but at this stage the presence of other galactose and mannose derivatives cannot be excluded.

We wish to thank Mr. L. J. Breddy for assistance in the preparation of the galactomannan.

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273. *Preparation and Properties of Allyl Phosphines, Arsines, and Stannanes.*

By W. J. JONES, W. C. DAVIES, S. T. BOWDEN, C. EDWARDS, V. E. DAVIS, and L. H. THOMAS.

Phosphines, arsines, and stannanes containing allyl and methylallyl groups have been produced by means of the Grignard reaction, their physical properties have been examined, and characteristic derivatives have been prepared.

No phosphine containing either an allyl or a methylallyl group has hitherto been prepared, though Hofmann (*Phil. Trans.*, 1860, **150**, 412) records that he experimented unsuccessfully on the effect of heating phosphorus, zinc, and allyl iodide together in a sealed tube, but phenyl-*p*-tolylmethylallylphosphonium iodide has been obtained by Pope and Gibson (*J.*, 1912, **101**, 737; also Radcliffe and Brindley, *J. Soc. Chem. Ind.*, 1923, **42**, 66) by the combination of phenyl-*p*-tolylmethylphosphine with allyl iodide, and trisdiphenylylallylphosphonium bromide by Worral (*J. Amer. Chem. Soc.*, 1930, **52**, 2936) by the union of trisdiphenylylphosphine and allyl bromide. Such phosphines have now been prepared by the Grignard method, *triallyl-phosphine* and *phenyl-*, p-*tolyl-*, p-*xylyl-*, p-*ethylphenyl-*, p-iso*propylphenyl-*, p-*methoxyphenyl-*, p-*phenoxyphenyl-*, and p-*bromophenyl-diallylphosphine* from allylmagnesium bromide, and *tri*-β-*methylallylphosphine* and *phenyl-*, p-*tolyl-*, p-*xylyl-*, p-*ethylphenyl-*, p-iso*propylphenyl-*, p-*methoxyphenyl-*, and p-*bromophenyl-di*-β-*methylallylphosphine* from β-methylallylmagnesium bromide.

Triallylarsine has been obtained by Gryszkiewicz-Trochimowski and Zambrzycki (*Rocz. Chem.*, 1926, **6**, 794). *Phenyldiallylarsine* has now been prepared from allylmagnesium bromide, and *tri*-β-*methylallylarsine* and *phenyldi*-β-*methylallylarsine* from β-methylallylmagnesium bromide.

Tetra-allyltin has been described by Vijayraghavan (*J. Indian Chem. Soc.*, 1945, **22**, 119), and allylstannonic acid and allylpentachlorostannic acid by Lesbre and Glotz (*Compt. rend.*, 1934, **198**, 1427). *Triethylallyltin, diethyldiallyltin, tri*-n-*butylallyltin* and *di*-n-*butyldiallyltin* have been prepared in the present work from allylmagnesium bromide.

In order to secure good yields, it has been found necessary to employ the Grignard reagent in excess over the chlorophosphine, chloroarsine, or chlorostannane, to exclude air rigorously during the preparation, and to distil the product under low pressure. In the reaction, diallyl, b. p. 59·5°, or di-β-methylallyl, b. p. 113°, is formed as by-product through the coupling action of the Grignard reagent, but the hydrocarbon is easily separated, after the ether, by distillation from the phosphine, arsine, or stannane.

The allylphosphines rapidly oxidise in contact with air. They combine with mercuric chloride to give mercurichlorides of the general formula $PR_3,HgCl_2$, with benzoquinone to produce pale yellow addition compounds $PR_3,C_6H_4O_2$, with carbon disulphide to yield either intensely red compounds PR_3,CS_2 or red colorations in solution, and with methyl iodide to give the methylphosphonium iodides. These methiodides combine with mercuric iodide to

form yellow complex mercuri-iodides PR_4I,HgI_2, and with cadmium iodide to give cadmi-iodides $(PR_4I)_2,CdI_2$. The allylarsines closely resemble the phosphines chemically, and the allylstannanes also are rapidly attacked by air.

In the absence of air, the allyl-phosphines, -arsines, and -stannanes are thermally stable, being unaffected even on being kept at 250° for an hour. A comparison of the b. p./50 mm. with that of the corresponding *n*-alkyl compound is made in the following table, from which it will be seen that the difference is slight.

Phosphine.	B. p./50 mm.	Phosphine.	B. p./50 mm.
Triallyl	98°	Tri-*n*-propyl	103°
Phenyldiallyl	160	Phenyldi-*n*-propyl	159
p-Tolyldiallyl	171	*p*-Tolyldi-*n*-propyl	174
p-Xylyldiallyl	179	*p*-Xylyldi-*n*-propyl	180
p-Ethylphenyldiallyl	188	*p*-Ethylphenyldi-*n*-propyl	181
Tri-β-methylallyl	142	Tri-*n*-butyl	149
Phenyldi-β-methylallyl	184	Phenyldi-*n*-butyl	185
p-Tolyldi-β-methylallyl	190	*p*-Tolyldi-*n*-butyl	197
p-Xylyldi-β-methylallyl	200	*p*-Xylyldi-*n*-butyl	204
p-Ethylphenyldi-β-methylallyl	205	*p*-Ethylphenyldi-*n*-butyl	209
Arsine.		**Arsine.**	
Triallyl	111	Tri-*n*-propyl	110
Phenyldiallyl	171	Phenyldi-*n*-propyl	165
Tri-β-methylallyl	143	Tri-*n*-butyl	155
Phenyldi-β-methylallyl	189	Phenyldi-*n*-butyl	193
Stannane.		**Stannane.**	
Triethylallyl	112	Triethyl-*n*-propyl	112

As is shown in the next table, the average difference between the molecular volumes (in c.c.) of an aryldiallylphosphine and its corresponding aryldi-β-methylallylphosphine at 25° is 34·0 c.c., compared with 33·0 c.c. for two CH_2 groups in the higher trialkylphosphines (Jackson, Davies, and Jones, *J.*, 1931, 2109).

Phosphine.	Diallyl.	Di-β-methylallyl.	Diff.
Phenyl	196·2	230·2	34·0
p-Tolyl	211·5	246·5	35·0
p-Xylyl	227·6	262·0	34·4
p-Ethylphenyl	230·0	263·2	33·2
p-*iso*Propylphenyl	248·0	280·6	32·6
p-Methoxyphenyl	216·2	249·6	33·4
p-Bromophenyl	210·6	245·8	35·2

The Lorenz–Lorentz molecular refractivities, $(n^2 - 1)M/(n^2 + 2)d$, of the allyl phosphines for sodium D light are given in the following table. The calculated values have been obtained by means of the constants given by Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 605), together with those given for phosphorus by Jones, Davies, and Dyke (*J. Physical Chem.*, 1933, **37**, 594).

	$[M_L]_D$.			$[M_L]_D$.	
Diallylphosphine.	Found.	Calc.	Di-β-methylallylphosphine.	Found.	Calc.
Phenyl	64·08	63·99	Phenyl	73·16	73·23
p-Tolyl	68·25	68·99	*p*-Tolyl	78·11	78·24
p-Xylyl	72·95	73·35	*p*-Xylyl	82·84	82·58
p-Ethylphenyl	73·78	73·82	*p*-Ethylphenyl	83·03	83·05
p-*iso*Propylphenyl	78·24	78·44	*p*-*iso*Propylphenyl	87·36	87·67
p-Methoxyphenyl	70·97	70·83	*p*-Methoxyphenyl	79·65	80·07
p-Phenoxyphenyl	89·47	89·76	*p*-Bromophenyl	81·23	80·99

The phosphines, arsines, and stannanes are freely soluble in ether, alcohol, benzene, or carbon tetrachloride, but not in water. The molecular weights, *M*, of the phosphines have been determined by the cryoscopic method in benzene solution, and found to be normal.

Experimental.

Preparation of the Phosphines.—The necessary dichlorophosphines, phenyl b. p. 221—222°, *p*-tolyl b. p. 100°/12 mm., *p*-xylyl b. p. 133°/16 mm., *p*-ethylphenyl b. p. 133°/18 mm., *p*-*iso*propylphenyl b. p. 132—134°/14 mm., *p*-methoxyphenyl b. p. 153°/21 mm., *p*-phenoxyphenyl b. p. 200°/12 mm., and *p*-bromophenyl b. p. 135—136°/14 mm., were prepared by the method of Michaelis (*Ber.*, 1879, **12**, 1009; *Annalen*, 1896, **293**, 223) and isolated either by the distillation method of Grüttner and Wiernik (*Ber.*, 1915, **48**, 1475) or by the extraction method of Davies (*J.*, 1935, 463). Allyl bromide,

b. p. 70—71°, was prepared as described in *Org. Synth.*, I, 24. To prepare β-methylallyl bromide, phosphorus tribromide (45 c.c.) was added dropwise with exclusion of moisture during 5 hours with periodic shaking to dried (CaO), freshly-distilled β-methylallyl alcohol (118 c.c.) in dried (KOH), freshly-distilled pyridine (32 c.c.) cooled with ice–salt: the reaction mixture was filtered, and the filtrate on distillation gave β-methylallyl bromide, b. p. 94—95° (85 g.). Both bromides after drying (P_4O_{10} or $CaCl_2$) were used immediately, after a fresh distillation, for the preparation of the phosphines.

To 1½ mols. (36·5 g.) of finely divided magnesium a granule of iodine and 100 c.c. of absolute ether, contained in a dried round-bottom flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, siphon tube, and a gas-inlet tube, through which dry hydrogen was passed, there was added, dropwise in the course of about 2 hours so as to maintain a gentle boiling, ½ mol. of allyl bromide (42 c.c.) or of β-methylallyl bromide (51 c.c.) in 285 c.c. of ether (Gilman and McGlumphy, *Bull. Soc. chim.*, 1928, **43**, 1322). After an hour's standing, the Grignard solution was siphoned quickly through a glass-wool filter into a second round-bottom flask provided with similar fittings to the first, and, with continuous stirring, passage of hydrogen and external cooling with ice, thereto was added gradually in ether (100 c.c.) 1/12 mol. of phosphorus trichloride (7·1 c.c.) or 1/8 mol. of the aryldichlorophosphine [phenyl (17 c.c.), *p*-tolyl (19 c.c.), *p*-xylyl (21 c.c.), *p*-ethylphenyl (21 c.c.), *p-iso*propylphenyl (22 c.c.), *p*-methoxyphenyl (20 c.c.), *p*-phenoxyphenyl (24 c.c.), or *p*-bromophenyl (19 c.c.)]. After the addition, the mixture was boiled for ½ hour, again cooled to 0°, and then ammonium chloride (50 g.) in water (250 c.c.) was added gradually through the dropping-funnel until all the precipitated magnesium salts had dissolved. The resulting mixture was siphoned under carbon dioxide into a separating funnel, and the ether layer was dried (Na_2SO_4) in a stoppered bottle. The dried solution was distilled in carbon dioxide to remove ether and diallyl or di-β-methylallyl, and the residual phosphine was redistilled in carbon dioxide under low pressure and preserved in sealed glass tubes. All subsequent manipulations of the phosphine were carried out under carbon dioxide.

Triallylphosphine.—This *compound* was prepared from allylmagnesium bromide and phosphorus trichloride; the liquid (4 g.) had b. p. 69°/13 mm. (Found: C, 70·1; H, 10·0; P, 19·7. $C_9H_{15}P$ requires C, 70·1; H, 9·8; P, 20·1%). Mercuric chloride added to the phosphine in alcohol precipitated the *mercurichloride*, rhomboids, m. p. 135° (Found: Cl, 16·9; P, 7·2. $C_9H_{15}P,HgCl_2$ requires Cl, 16·7; P, 7·3%). This and all the succeeding mercurichlorides, mercuri-iodides and cadmi-iodides were repeatedly recrystallised to constant m. p. from alcohol, except where another solvent is stated.

The phosphine (1 c.c.) in alcohol (20 c.c.) mixed with *p*-benzoquinone (0·4 g.) in alcohol (20 c.c.) produced a red coloration, and after standing, the addition of ether precipitated pale-yellow stellate crystals of *triallylphosphine–p-benzoquinone*, which darkened at 100° and became black at 130° (Found: C, 69·1; H, 7·5. $C_{15}H_{19}O_2P$ requires C, 68·7; H, 7·3%). Excess of carbon disulphide added to the phosphine (2 c.c.) in alcohol (5 c.c.) gave a dark red coloration, and on cooling to 0° *triallylphosphine–carbondisulphide* separated as red needles, m. p. 32·5°, unstable in the air (Found: C, 51·7; H, 6·9. $C_{10}H_{15}PS_2$ requires C, 52·1; H, 6·6%). Mixed in the absence of air, the phosphine and methyl iodide in ether immediately gave a precipitate of *methyltriallylphosphonium iodide*, pearly flakes from alcohol–ether (Found: I, 42·7. $C_{10}H_{18}PI$ requires I, 42·9%).

Phenyldiallylphosphine.—This *compound* (8 g.) was obtained by the interaction of allylmagnesium bromide and phenyldichlorophosphine and had b. p. 127°/14 mm., $d_4^{25°}$ 0·9693, $n_D^{25°}$ 1·5670 (Found: C, 75·5; H, 8·1. $C_{12}H_{15}P$ requires C, 75·7; H, 8·0%). It formed the *mercurichloride*, needles, m. p. 123° (Found: Cl, 15·6. $C_{12}H_{15}P,HgCl_2$ requires Cl, 15·4%).

p-*Tolyldiallylphosphine.*—The *phosphine* (7 g.) was produced from allylmagnesium bromide and *p*-tolyldichlorophosphine and had b. p. 138°/14 mm., $d_4^{25°}$ 0·9651, $n_D^{25°}$ 1·5545 (Found: C, 75·9; H, 8·9. $C_{13}H_{17}P$ requires C, 76·4; H, 8·4%). It yielded the *mercurichloride*, elongated prisms, m. p. 110·5° (Found: Cl, 14·9. $C_{13}H_{17}P,HgCl_2$ requires Cl, 14·9%).

p-*Xylyldiallylphosphine.*—The interaction of the allyl Grignard reagent and *p*-xylyldichlorophosphine gave the *phosphine* (16 g.), which had b. p. 144°/13 mm., $d_4^{25°}$ 0·9584, $n_D^{25°}$ 1·5540 (Found: C, 76·6; H, 8·8; P, 14·0; *M*, 223. $C_{14}H_{19}P$ requires C, 77·0; H, 8·8; P, 14·2%; *M*, 218). The *mercurichloride* crystallised in rhomboids, m. p. 170° (Found: Cl, 14·9; P, 6·3. $C_{14}H_{19}P,HgCl_2$ requires Cl, 14·5; P, 6·3%).

p-*Ethylphenyldiallylphosphine.*—Obtained from allylmagnesium bromide and *p*-ethylphenyldichlorophosphine, the *phosphine* (16 g.) had b. p. 145°/10 mm., $d_4^{25°}$ 0·9484, $n_D^{25°}$ 1·5545 (Found: C, 76·7; H, 9·0. $C_{14}H_{19}P$ requires C, 77·0; H, 8·8%).

p-iso*Propylphenyldiallylphosphine.*—This *compound* (16 g.) was prepared from allylmagnesium bromide and *p-iso*propylphenyldichlorophosphine and had b. p. 153°/11 mm., $d_4^{25°}$ 0·9361, $n_D^{25°}$ 1·5435 (Found: C, 77·5; H, 9·1; *M*, 242. $C_{15}H_{21}P$ requires C, 77·5; H, 9·1%; *M*, 232). It yielded the *mercurichloride*, m. p. 47°, from glacial acetic acid (Found: Cl, 14·6. $C_{15}H_{21}P,HgCl_2$ requires Cl, 14·1%).

p-*Methoxyphenyldiallylphosphine.*—This *phosphine* (12 g.), produced from allylmagnesium bromide and *p*-methoxyphenyldichlorophosphine, had b. p. 162°/15 mm., $d_4^{25°}$ 1·0189, $n_D^{25°}$ 1·5705 (Found: C, 70·6; H, 8·1. $C_{13}H_{17}OP$ requires C, 70·9; H, 7·8%). Its *mercurichloride* separated in prisms, m. p. 131° (Found: Cl, 14·8. $C_{13}H_{17}OP,HgCl_2$ requires Cl, 14·4%).

p-*Phenoxyphenyldiallylphosphine.*—Obtained by the action of the allyl Grignard reagent on *p*-phenoxyphenyldichlorophosphine, this *phosphine* (12 g.) had b. p. 238°/15 mm., $d_4^{25°}$ 1·0847, $n_D^{25°}$ 1·6040 (Found: C, 76·2; H, 7·1; P, 10·9; *M*, 278. $C_{18}H_{19}OP$ requires C, 76·6; H, 6·8; P, 11·0%; *M*, 282). The *mercurichloride*, difficultly soluble in alcohol and ether, became black at 210° (Found: Cl, 13·2. $C_{18}H_{19}OP,HgCl_2$ requires Cl, 12·8%).

p-*Bromophenyldiallylphosphine.*—The allyl Grignard reagent and *p*-bromophenyldichlorophosphine gave the *phosphine* (15 g.), b. p. 186°/37 mm., $d_4^{25°}$ 1·2783 (Found: C, 53·1; H, 5·5; P, 11·4; *M*, 272. $C_{12}H_{14}BrP$ requires C, 53·5; H, 5·2; P, 11·5%; *M*, 269). The *mercurichloride* crystallised in needles, m. p. 108° (Found: P, 5·7. $C_{12}H_{14}BrP,HgCl_2$ requires P, 5·7%).

Tri-β-methylallylphosphine.—This tertiary *phosphine* (5 g.) was prepared through the interaction of β-methylallylmagnesium bromide and phosphorus trichloride and had b. p. 112°/15 mm. (Found:

C, 73·1; H, 11·0; P, 15·4; *M*, 196. $C_{12}H_{21}P$ requires C, 73·4; H, 10·8; P, 15·8%; *M*, 196). It immediately oxidised in the air to form the *oxide*, needles, m. p. 132°, from ether (Found: C, 67·6; H, 10·2. $C_{12}H_{21}OP$ requires C, 67·9; H, 10·0%); the same compound was also produced from β-methylallylmagnesium bromide and phosphorus oxychloride. In the absence of air the phosphine and mercuric chloride in alcohol gave *tri-β-methylallylphosphine mercurichloride*, rhombic plates, m. p. 162° (Found: Cl, 15·2. $C_{12}H_{21}P,HgCl_2$ requires Cl, 15·2%). *Methyltri-β-methylallylphosphonium iodide*, from its components in ether, formed needles, m. p. 151°, from alcohol–ether (Found: I, 37·4. $C_{13}H_{24}PI$ requires I, 37·5%). *Tri-β-methylallylphosphine–p-benzoquinone*, precipitated by ether from mixed alcoholic solutions of its components, formed pale lemon-yellow stellate crystals, which darkened in the air or on heating, becoming black at 200° (Found: C, 70·8; H, 8·5. $C_{18}H_{25}O_2P$ requires C, 71·0; H, 8·3%).

Phenyldi-β-methylallylphosphine.—The *compound* (15 g.) was obtained from the Grignard reagent and phenyldichlorophosphine, and had b. p. 148°/13 mm., $d_4^{25°}$ 0·9484, $n_D^{25°}$ 1·5485 (Found: C, 76·8; H, 9·0; P, 14·2; *M*, 223. $C_{14}H_{19}P$ requires C, 77·0; H, 8·8; P, 14·2%; *M*, 218). It gave the *mercurichloride*, rectangular plates, m. p. 140·5° (Found: Cl, 14·7. $C_{14}H_{19}P,HgCl_2$ requires Cl, 14·5%). *Phenylmethyldi-β-methylallylphosphonium iodide* separated in needles, m. p. 188° (decomp.), from alcohol–ether (Found: I, 34·9. $C_{15}H_{22}PI$ requires I, 35·2%). On mixing hot alcoholic solutions of mercuric iodide and excess of the methiodide, *phenylmethyldi-β-methylallylphosphonium mercuri-iodide* crystallised out on cooling as lemon-coloured needles, m. p. 133° (Found: I, 47·0; Hg, 24·5. $C_{15}H_{22}PI,HgI_2$ requires I, 46·7; Hg, 24·6%). Similarly, cadmium iodide and the methiodide gave the *cadmi-iodide*, needles, m. p. 114° [Found: I, 46·7; Cd, 10·5. $(C_{15}H_{22}PI)_2,CdI_2$ requires I, 46·7; Cd, 10·3%]. Addition of excess of bromine to the phosphine in ether gave a precipitate, which, on solution in hot alcohol and treatment with water until turbidity appeared, yielded *phenyldi-(βγ-dibromo-β-methylpropyl)phosphine oxide*, needles, m. p. 105°, from aqueous alcohol (Found: Br, 57·6. $C_{14}H_{19}OBr_4P$ requires Br, 57·7%).

p-*Tolyldi-β-methylallylphosphine.*—Prepared from the β-methylallyl Grignard reagent and *p*-tolyldichlorophosphine, the *phosphine* (11 g.) had b. p. 168°/23 mm., $d_4^{25°}$ 0·9426, $n_D^{25°}$ 1·5465 (Found: C, 77·4; H, 9·3; P, 13·3; *M*, 228. $C_{15}H_{21}P$ requires C, 77·5; H, 9·1; P, 13·4%; *M*, 232). It gave the *mercurichloride*, cubes, m p. 164° (Found: Cl, 14·2. $C_{15}H_{21}P,HgCl_2$ requires Cl, 14·1%). p-*Tolylmethyldi-β-methylallylphosphonium iodide* crystallised in needles, m. p. 94°, from alcohol–ether (Found: I, 33·8. $C_{16}H_{24}PI$ requires I, 33·9%) and yielded p-*tolylmethyldi-β-methylallylphosphonium mercuri-iodide*, pale-yellow prisms, m. p. 79° (Found: I, 46·1; Hg, 24·1. $C_{16}H_{24}PI,HgI_2$ requires I, 45·9; Hg, 24·2%).

p-*Xylyldi-β-methylallylphosphine.*—The *phosphine* (12 g.) was obtained from β-methylallylmagnesium bromide and *p*-xylyldichlorophosphine; it had b. p. 166°/16 mm., $d_4^{25°}$ 0·9402, $n_D^{25°}$ 1·5450 (Found: C, 77·8; H, 9·4; P, 12·3. $C_{16}H_{23}P$ requires C, 78·0; H, 9·4; P, 12·6%). The *mercurichloride* separated in prisms, m. p. 201—202° (Found: Cl, 13·7. $C_{16}H_{23}P,HgCl_2$ requires Cl, 13·7%). p-*Xylylmethyldi-β-methylallylphosphonium iodide* crystallised in prisms, m. p. 161°, from alcohol–ether (Found: I, 32·5. $C_{17}H_{26}PI$ requires I, 32·7%). It gave with mercuric iodide in alcohol the *mercuri-iodide*, pale yellow rhombic plates, m. p. 71° (Found: I, 45·5; Hg, 23·6. $C_{17}H_{26}PI,HgI_2$ requires I, 45·2; Hg, 23·8%), and with cadmium iodide, the *cadmi-iodide*, needles, m. p. 159° [Found: I, 44·0; Cd, 10·2. $(C_{17}H_{26}PI)_2,CdI_2$ requires I, 44·4; Cd, 9·8%].

p-*Ethylphenyldi-β-methylallylphosphine.*—This *compound* (12 g.), prepared from the Grignard reagent and *p*-ethylphenyldichlorophosphine, had b. p. 178°/20 mm., $d_4^{25°}$ 0·9360, $n_D^{25°}$ 1·5435 (Found: C, 77·7; H, 9·6; P, 12·4; *M*, 240. $C_{16}H_{23}P$ requires C, 78·0; H, 9·4; P, 12·6%; *M*, 246). The *mercurichloride* separated in prisms, m. p. 156° (Found: Cl, 14·1. $C_{16}H_{23}P,HgCl_2$ requires Cl, 13·7%). p-*Ethylphenylmethyldimethyl-β-allylphosphonium iodide*, rectangular plates, m. p. 153°, from alcohol–ether (Found: I, 32·4. $C_{17}H_{26}PI$ requires I, 32·7%), gave the *mercuri-iodide*, pale yellow needles, m. p. 82·5° (Found: I, 45·3; P, 23·5. $C_{17}H_{26}PI,HgI_2$ requires I, 45·2; P, 23·8%).

p-iso*Propylphenyldi-β-methylallylphosphine.*—Interaction of the Grignard reagent and *p-iso*propylphenyldichlorophosphine gave the *phosphine* (14 g.), b. p. 182·5°/19 mm., $d_4^{25°}$ 0·9279, $n_D^{25°}$ 1·5350 (Found: C, 77·9; H, 9·8; P, 11·8; *M*, 263. $C_{17}H_{25}P$ requires C, 78·4; H, 9·7; P, 11·9%; *M*, 260). Its *mercurichloride* was obtained in needles, m. p. 153° (Found: Cl, 13·4. $C_{17}H_{25}P,HgCl_2$ requires Cl, 13·3%).

p-*Methoxyphenyldi-β-methylallylphosphine.*—*p*-Methoxyphenyldichlorophosphine and di-β-methylallylmagnesium bromide reacted to give the *phosphine* (12 g.), b. p. 192°/20 mm., $d_4^{25°}$ 0·9948, $n_D^{25°}$ 1·5513 (Found: C, 72·3; H, 8·7. $C_{15}H_{21}OP$ requires C, 72·6; H, 8·6%). Its *mercurichloride* separated in cubes, m. p. 181° (Found: Cl, 13·8. $C_{15}H_{21}OP,HgCl_2$ requires Cl, 13·6%). p-*Methoxyphenylmethyldi-β-methylallylphosphonium iodide*, needles, m. p. 134·5°, from water (Found: I, 32·3. $C_{16}H_{24}OPI$ requires I, 32·5%) gave the *mercuri-iodide*, pale yellow prisms, m. p. 71° (Found: I, 45·0; Hg, 23·7. $C_{16}H_{24}OPI,HgI_2$ requires I, 45·1; Hg, 23·7%), and the *cadmi-iodide*, needles, m. p. 132° [Found: I, 44·2; Cd, 10·1. $(C_{16}H_{24}OPI)_2,CdI_2$ requires I, 44·3; Cd, 9·8%].

p-*Bromophenyldi-β-methylallylphosphine.*—Obtained from di-β-methylallylmagnesium bromide and *p*-bromophenyldichlorophosphine, this *phosphine* (14 g.) had b. p. 189°/18 mm., $d_4^{25°}$ 1·2094, $n_D^{25°}$ 1·5752 (Found: C, 56·7; H, 6·3; P, 10·3; *M*, 293. $C_{14}H_{18}BrP$ requires C, 56·6; H, 6·1; P, 10·4%; *M*, 297). The *mercurichloride* was obtained in cubes, m. p. 194° (Found: Cl, 12·4. $C_{14}H_{18}BrP,HgCl_2$ requires Cl, 12·5%). p-*Bromophenylmethyldi-β-methylallylphosphonium iodide*, cubes, m. p. 174°, from alcohol–ether (Found: I, 28·8. $C_{15}H_{21}BrPI$ requires I, 28·9%), yielded the *mercuri-iodide*, pale yellow needles, m. p. 67° (Found: I, 42·8; Hg, 22·4. $C_{15}H_{21}BrPI,HgI_2$ requires I, 42·6; Hg, 22·4%) and the *cadmi-iodide*, needles, m. p. 178° [Found: I, 40·8; Cd, 9·3. $(C_{15}H_{21}BrPI)_2,CdI_2$ requires I, 40·8; Cd, 9·0%]. On adding bromine to the phosphine in ether until a brown colour persisted, there was deposited an oil which solidified on being kept in a vacuum; on dissolving the solid in alcohol, adding water until turbidity developed, and allowing the mixture to stand, there formed crystals of p-*bromophenyldi-(βγ-dibromo-β-methylpropyl)phosphine oxide*, needles, m. p. 152°, from alcohol (Found: C, 26·6; H, 2·9; Br, 63·2; non-nuclear Br, 51·3. $C_{14}H_{18}OBr_5P$ requires C, 26·6; H, 2·9; Br, 63·1; non-nuclear Br, 50·5%).

Preparation of the Arsines.—To the allyl or β-methylallyl Grignard reagent, prepared as already described, was added arsenic trichloride (6·8 c.c.) in ether (50 c.c.) or phenyldi-iodoarsine (51 g., obtained by the method of Steinkopf and Smie, *Ber.*, 1926, **59**, 1461) in ether (200 c.c.). The isolation and purification of the arsine were also effected by redistillation under low pressure in carbon dioxide.

Phenyldiallylarsine.—This *arsine* (9 g.) was prepared by the interaction of allylmagnesium bromide and phenyldi-iodoarsine; it had b. p. 131°/10 mm. (Found: C, 61·3; H, 6·4; As, 31·3. $C_{12}H_{15}As$ requires C, 61·5; H, 6·5; As, 32·0%). It formed the *mercurichloride*, needles, m. p. 120° (Found: Cl, 13·8. $C_{12}H_{15}As,HgCl_2$ requires Cl, 14·0%).

Tri-β-methylallylarsine.—The *compound* (6 g.), obtained from β-methylallylmagnesium bromide and arsenic trichloride, had b. p. 114°/15 mm. (Found: C, 59·3; H, 8·7; As, 31·4. $C_{12}H_{21}As$ requires C, 60·0; H, 8·8; As, 31·2%). It yielded the *mercurichloride*, needles, m. p. 96—97° (decomp.), from glacial acetic acid (Found: Cl, 14·2. $C_{12}H_{21}As,HgCl_2$ requires Cl, 13·9%), and *methyltri-β-methylallylarsonium iodide*, long rectangles, m. p. 129° (slight decomp.), from alcohol (Found: I, 33·0. $C_{13}H_{24}AsI$ requires I, 33·2%).

Phenyldi-β-methylallylarsine.—Interaction of the β-methylallyl Grignard reagent and phenyldi-iodoarsine gave the *arsine* (15 g.), b. p. 153°/13 mm., $d_4^{25°}$ 1·1200 (Found: C, 63·7; H, 7·5; As, 28·7. $C_{14}H_{19}As$ requires C, 64·1; H, 7·3; As, 28·6%). It formed *phenylmethyldi-β-methylallylarsonium iodide*, needles, m. p. 163° (slight decomp.), from water (Found: I, 31·4. $C_{15}H_{22}AsI$ requires I, 31·4%).

Preparation of the Stannanes.—Triethylchlorotin, b. p. 209—210°, and diethyldichlorotin, m. p. 84°, were obtained by the methods of Kocheshkov (*J. Gen. Chem. Russia*, 1934, **4**, 1359; 1935, **5**, 211). *Tri*-n-*butylchlorotin* (40 g.) was prepared by heating (oil-bath) a mixture of tetra-*n*-butyltin (39 c.c.) and tin tetrachloride (4·6 c.c.) at 230° for 3 hours, and fractionating the product under low pressure; it had b. p. 172°/25 mm. (Found: Cl, 11·1. $C_{12}H_{27}SnCl$ requires Cl, 10·9%). *Di*-n-*butyldichlorotin* (20 g.) was obtained by heating a mixture of tetra-*n*-butyltin (16·5 c.c.) and tin tetrachloride (5·9 c.c.) for 3 hours at 240°, and recrystallising the product from light petroleum with cooling to − 20°; it formed plates, m. p. 40·5° (Found: Cl, 23·3. $C_8H_{18}SnCl_2$ requires Cl, 23·3%).

The chlorotin in benzene or ether was added to the allyl Grignard solution under hydrogen. After removal of the solvent and diallyl by distillation in carbon dioxide, the residue was dissolved in benzene (80 c.c.), the solution shaken with dilute sodium hydroxide solution to remove any traces of chloro-compound and then dried ($CaCl_2$), and the stannane isolated by distillation under low pressure in carbon dioxide.

Triethylallyltin.—This *compound* (21 g.) was prepared from the allyl Grignard solution and triethylchlorotin (30 g.) in benzene (90 c.c.), and had b. p. 76—77°/10 mm. (Found: C, 43·9; H, 8·3; Sn, 48·0. $C_9H_{20}Sn$ requires C, 43·8; H, 8·1; Sn, 48·1%).

Diethyldiallyltin.—Obtained by the action of the Grignard solution on diethyldichlorotin (16·8 g.) in benzene (60 c.c.), this *compound* (9 g.) had b. p. 99—100°/17 mm. (Found: C, 46·0; H, 7·7; Sn. 45·9. $C_{10}H_{20}Sn$ requires C, 46·3; H, 7·8; Sn, 45·9%).

Tri-n-*butylallyltin.*—The interaction of allylmagnesium bromide and tri-*n*-butylchlorotin (40 g.) in ether (120 c.c.) gave this *compound* as a liquid (30 g.), b. p. 155°/17 mm. (Found: C, 54·1; H, 9·8. $C_{15}H_{32}Sn$ requires C, 54·4; H, 9·8%).

Di-n-*butyldiallyltin.*—This *compound* (9·6 g.), prepared from the Grignard reagent and di-*n*-butyldichlorotin (19 g.) in ether (60 c.c.), had b. p. 145—146°/17 mm. (Found: C, 53·2; H, 9·1. $C_{14}H_{28}Sn$ requires C, 53·2; H, 9·0%).

The following derivatives were also prepared. *Ethyltrichlorotin* (6 g.) was obtained by refluxing tetraethyltin (7·9 c.c.) and tin tetrachloride (42 c.c.) for 24 hours and fractionating the product; it had b. p. 196—198° (Found: Cl, 42·3. $C_2H_5SnCl_3$ requires Cl, 41·9%). After standing, a solution of 15 g. of allylstannonic acid (Found: Sn, 62·4. Calc. for $C_3H_6O_2Sn$: Sn, 61·5%) in a mixture of 50 c.c. of hydrobromic acid (*d* 1·5) and 50 c.c. of water deposited 40 g. of *allylpentabromostannic acid* (Found: Br, 71·2. $C_3H_7Br_5Sn$ requires Br, 71·2%); it separated in small, pale yellow cubes, soluble in water but not in organic solvents, and decomposed on heating.

The physical measurements here recorded were carried out with standardised apparatus, and all relevant corrections were applied. The yields given are not of crude, but of fully purified substance. Combustions were carried out by using lead chromate–copper oxide mixtures, determinations of phosphorus by the method of Davies and Davies (*J.*, 1931, 1207), of arsenic by that of Lewis and Davis (*J.*, 1939, 286), of tin by that of Gilman and King (*J. Amer. Chem. Soc.*, 1929, **51**, 1213), and of mercury, cadmium, and iodine in complex salts by the method of Mannheim (*Annalen*, 1905, **341**, 192).

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274. *Bromination of Dimethoxystilbenes.*

By FELIX BERGMANN and HELENE JAPHÉ.

2 : 2′- and 3 : 3′-Dimethoxystilbene can be converted in a two-step process into symmetrical dibromodimethoxystilbenes. The 2 : 2′-compound is substituted in positions 5 and 5′.

IN a recent publication (Bergmann and Schapiro, *J. Org. Chem.*, 1947, **12**, 57) it was reported that 2-methoxystilbene undergoes nuclear bromination with such ease that in place of the expected dibromide there was obtained 5-bromo-2-methoxystilbene dibromide. We have now extended this observation to symmetrical dimethoxystilbenes.

Auwers (*Ber.*, 1903, **36**, 1888), using excess of bromine, converted 4 : 4′-dimethoxystilbene into 3 : 5 : 3′ : 5′-tetrabromo-4 : 4′-dimethoxystilbene dibromide. In this case, both positions

ortho to the methoxyl group are equivalent, whereas the para position is substituted by an olefinic chain. However, no disturbing effect is to be expected from this chain, as in all known cases the speed of addition of bromine to the central double bond of a stilbene is greater than that of nuclear substitution. The CHBr group is unlikely to exert any influence on this latter reaction, because Bance, Barber, and Woolman (*J.*, 1943, 1) observed the complete inertness of stilbene dibromide towards bromination in the ring. Therefore we assumed that in 2 : 2′-dimethoxystilbene dibromide the methoxy-groups would direct the attack of bromine exclusively. This was borne out by experiment.

After saturation of the double bond of 2 : 2′-dimethoxystilbene by bromine, substitution proceeded slowly, and although exactly 3 mols. of bromine were added, the reaction product was a mixture which could not be separated. It was, therefore, treated directly with potassium iodide. The mixture of bromostilbenes, so obtained, could be separated by fractional crystallisation into two substances of m. p. 214° and 130°, severally, which upon addition of 1 mol. of bromine yielded " dibromides " of m. p. 256° and 225° respectively. The compound of m. p. 214° is a dibromo-2 : 2′-dimethoxystilbene and was identified as the 5 : 5′-dibromo-derivative by direct comparison with an authentic specimen (Ashley and Harris, *J.*, 1946, 567).

The substance of m. p. 130° contains only one bromine atom. That it was 5-*bromo*-2 : 2′-*dimethoxystilbene* was proved by its conversion *via* its *dibromide* into 5 : 5′-dibromo-2 : 2′-dimethoxystilbene dibromide. The reason for the incomplete conversion of 2 : 2′-dimethoxystilbene into the latter is to be found in the low reaction velocity. The monobromo-dibromide is sparingly soluble in chloroform, and if the bromine solution is added slowly, this compound has time to crystallise out, thus avoiding further bromination in the second ring. The preparation of the dibrominated bromide in nearly quantitative yield is, however, achieved easily, if excess bromine is added *at once* to a very dilute chloroform solution of 2 : 2′-dimethoxystilbene This method thus presents a much easier route to 5 : 5′-dibromo-2 : 2′-dimethoxystilbene than the procedure of Ashley and Harris (*loc. cit.*).

3 : 3′-Dimethoxystilbene is converted smoothly into a dibromo-3 : 3′-dimethoxystilbene dibromide and hence into the corresponding stilbene; by analogy, these are deemed to be the 2 : 2′-*dibromo*-5 : 5′-*dimethoxy*-compounds, although we were unable to oxidise the stilbene to the expected 2-bromo-5-methoxybenzoic acid.

Experimental.

2 : 2′-*Dimethoxystilbene*.—By the procedure of Baumann and Fromm (*Ber.*, 1891, **24**, 1441), the required *o*-methoxythiobenzaldehyde is obtained mainly as a tough syrup and crystallizes only partly. However, the syrupy mass gave as good a yield (*ca.* 30%) upon thermal decomposition as did the crystalline portion. The crude stilbene was purified by distillation, b. p. 180—190°/0·5 mm., and then crystallized quickly upon trituration with methanol. It formed clusters of needles from butanol and prisms from toluene; m. p. 140°.

Bromination. (1) The stilbene (0·7 g.) was dissolved in chloroform (5 c.c.), and bromine (1·4 g.; 3 mols.) in the same solvent (5 c.c.) was added dropwise during 5 mins. The first third was decolorised instantaneously, then the speed of reaction slackened, and after addition of the second third of bromine a precipitate appeared. Decolorisation of the last third of bromine was very slow and was completed by warming on a water-bath. After the evolution of hydrogen bromide had ceased, the solvent was evaporated and the residue treated with methanol; yield 1·3 g., m. p. 218—220°. The product was not homogeneous, and crystallisation from xylene did not give a pure compound. It was, therefore, suspended in acetone (25 c.c.) and heated under reflux with sodium iodide (1 g.) for 3 hours. After evaporation of the solvent and addition of thiosulphate, a white substance was obtained. Upon recrystallisation from toluene, appeared first needles, then plates. They were separated by fractional crystallisation. The needles finally had m. p. 214° (Found : C, 48·4; H, 3·6. Calc. for $C_{16}H_{14}O_2Br_2$: C, 48·2; H, 3·5%) and were identified (mixed m. p.) as 5 : 5′-dibromo-2 : 2′-dimethoxystilbene described by Ashley and Harris (*loc. cit.*). The plates, recrystallised from *iso*propanol and then from light petroleum (b. p. 80°), formed glistening, elongated plates, m. p. 130° (Found : C, 60·0; H, 4·7. $C_{16}H_{15}O_2Br$ requires C, 60·2; H, 4·7%), of the *monobromostilbene*.

(2) 2 : 2′-Dimethoxystilbene (0·8 g.) was treated with bromine (2 mols.) in chloroform solution, and the product triturated with light petroleum. The *5-bromo-dibromide* (1·6 g.; 100%) crystallised from toluene in colourless parallelepipeds with cut-off ends, m. p. 225° (Found : C, 39·8; H, 3·2. $C_{16}H_{13}O_2Br_3$ requires C, 40·1; H, 3·1%). It was identical with the compound formed by addition of bromine to the above monobromostilbene, into which it was converted by debromination with sodium iodide in acetone.

When the monobromostilbene was dissolved in chloroform and treated *at once* with excess of bromine, the dibromo-dibromide, m. p. 244° (see below), resulted.

(3) To 2 : 2′-dimethoxystilbene (6 g.; 1/40 mol.) in chloroform (50 c.c.) was added *at once* a solution of excess of bromine (20 g.; 5/40 mol.) in chloroform (50 c.c.), and the solution left overnight. The crude product (13·5 g.; 97%) had m. p. 244° and was difficult to recrystallise in greater amounts, because of decomposition. Small samples could be recrystallised from acetic anhydride, large volumes of xylene, or nitrobenzene. The products then showed different m. p.s; *e.g.*, from xylene prisms of m. p. 245°, and from nitrobenzene of m. p. 256°. All these samples of 5 : 5′-*dibromo*-2 : 2′-*dimethoxystilbene dibromide*

showed identical analyses (Found: C, 34·2; H, 2·6. $C_{16}H_{14}O_2Br_4$ requires C, 34·4; H, 2·5%) and were quantitatively converted into the corresponding stilbene by debromination with sodium iodide or by the cuprous chloride–pyridine procedure of Bance *et al.* (*loc. cit.*).

3 : 3′-*Dimethoxystilbene.*—The desulphuration of *m*-methoxythiobenzaldehyde started at 200° and was completed by heating to 230° for 35 mins. The crude reaction product was mixed with an equal weight of copper-bronze and distilled in a vacuum; b. p. 180—182°/0·1 mm. The distillate crystallised spontaneously. From *iso*propanol it formed prismatic plates, m. p. 101°; yield 10%.

Bromination. To the stilbene (1·3 g.) in chloroform (10 c.c.) was added dropwise a solution of bromine (2·6 g.) in chloroform (8·3 c.c.). When addition was complete, 2 : 2′-*dibromo*-5 : 5′-*dimethoxystilbene dibromide* crystallised out. The solvent was evaporated, and the residue treated with ethanol; yield 2·7 g. (90%). From acetic anhydride the substance crystallises in hexagonal plates, m. p. 236° (Found: C, 34·6; H, 2·5. $C_{16}H_{14}O_2Br_4$ requires C, 34·4; H, 2·5%). Debromination with potassium iodide in acetone, as above, gave a 90% yield of 2 : 2′-*dibromo*-5 : 5′-*dimethoxystilbene*, which crystallised from toluene as prismatic rods, m. p. 154—155° (Found: C, 48·3; H, 3·7. $C_{16}H_{14}O_2Br_2$ requires C, 48·2; H, 3·5%).

The authors wish to thank Dr. J. N. Ashley, who carried out the comparison of 5 : 5′-dibromo-2 : 2′-dimethoxystilbene with an authentic specimen, prepared by him.

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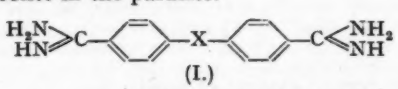
275. *Benzylamine Analogues of Chemotherapeutic Diamidines.*

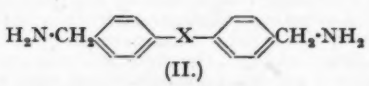
By ADRIEN ALBERT, JOHN A. MILLS, and RICHARD ROYER.

To help trace the origins of the outstanding chemotherapeutic properties of aromatic diamidines of type (I), the simpler bases of type (II) were synthesised for the first time.

THE researches of Ewins and his colleagues (cf. Ashley, Barber, Ewins, Newbery, and Self, *J.*, 1942, 103) established that aromatic diamidines of type (I), especially *c*, *d*, *e*, and *f*, have outstanding antiparasitic properties against protozoa. It is not known (i) whether the anti-protozoal activity of these substances is derived largely from their having two well-ionized and mutually independent basic groups held at a distance from one another, or (ii) whether such activity depends specifically on the amidine group which may conceivably function by assisting adsorption, through the resonance of its ion, or by interfering with a similarly constituted metabolite in the parasite.



(I.)



(II.)

(*a*) X absent; (*b*) X = CH_2; (*c*) X = O;
(*d*) X = O·$[CH_2]_3$·O; (*e*) X = O·$[CH_2]_5$·O; (*f*) X = CH=CH.

At this stage we propose only to examine hypothesis (i). This cannot be tested simply by replacing each amidine group by an amino-group because the basic strength of the latter would be enormously lowered through interaction with the benzene ring (cf. aniline and methylamine, Table I), leading to an almost complete absence of kations in neutral solution. If, however, the amino-group is insulated from the aromatic ring by a methylene group, the base-weakening resonance is repressed and a high degree of ionization results (cf. benzylamine and methylamine, Table I). That the ionization of amidines is little affected by the presence of an aromatic substituent is now shown for the first time (Table I).

TABLE I.

Ionisation of certain bases under physiological conditions.

Compound.	pK_a, 20° (water).	Source of value.	% ionized pH 7.
Acetamidine	12·52	A	100
Benzamidine	11·6 (M/10)	B	100
Methylamine	10·76	C	100
Aniline	4·65	D	0·5
Benzylamine	9·4	E	99·5

A. Schwarzenbach and Lutz, *Helv. Chim. Acta*, 1940, **23**, 1162.
B. Determined potentiometrically by Mr. R. Goldacre (for details of method, see Albert and Goldacre, *J.*, 1946, 706).
C. Britton and Williams, *J.*, 1935, 796.
D. Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.
E. Carothers, Bickford, and Hurwitz, *ibid.*, 1927, **49**, 2908.

The preparation of the bisbenzylamine compounds (II, *a*—*f*) was accordingly undertaken to permit of biological comparison with the corresponding diamidines (I), in particular with *c* (Phenamidine), *d* (Propamidine), *e* (Pentamidine), and *f* (Stilbamidine).

The corresponding dinitriles were hydrogenated by the method of Schwoegler and Adkins (*J. Amer. Chem. Soc.*, 1939, **61**, 3499) for aliphatic amines, methanolic ammonia being used in the presence of Raney-nickel catalyst at 110° for 20 minutes under 1200 lb./sq. in. pressure. In this way were prepared *pp'*-bisaminomethyldiphenyl (II, *a*), pp'-*bisaminomethyldiphenylmethane* (II, *b*), characterized as its *dibenzoyl* derivative, pp'-*bisaminomethyldiphenyl ether* (II, *c*), 1 : 3-(pp'-*bisaminomethyldiphenoxy*)*propane* (II, *d*), 1 : 5-(pp'-*bisaminomethyldiphenoxy*)-*pentane* (II, *e*), and pp'-*bisaminomethylstilbene* (II, *f*).

Before attempting the reduction of 4 : 4'-dicyanostilbene, it was confirmed that these conditions were not severe enough to reduce the double bond in *trans*-4 : 4'-diaminostilbene. The latter was made by reducing the mixture of dinitro- and dinitroso-stilbenes formed by the violent reaction of *p*-nitrotoluene and methanolic sodium hydroxide (Fischer and Hepp, *Ber.*, 1893, **26**, 2232). The mechanism of this reaction was investigated by Green, Davies, and Horsfall (*J.*, 1907, **91**, 2076), but no yields were given. As insufficient details exist in the literature for the safe and successful conduct of this reaction for preparative purposes, a detailed account is given in the experimental section.

The products (II, *a*—*f*) are white, water-insoluble solids which absorb carbon dioxide rapidly from the air but are stable in the form of their white, readily crystallising salts, of which the diacetates are more soluble than the dihydrochlorides and are to be preferred for biological work. That these substances possess the predicted basic strength may be inferred from the example quoted in Table II. This table also shows that, both here and in the diamidines, the two basic groups are too far apart for the ionization of the first to exert an adverse Coulombic effect on that of the second, such as is seen in trimethylenediamine (pK_a 9·8 and 7·0).

TABLE II.

Ionisation of certain diacid bases.

Compound.	pK_a values, 20° (50% ethanol).	Source of value.	Approx. % ionised in water at pH 7.
" Propamidine " (I, *d*)	11·6 & 10·8 (M/300)	B (see Table I)	100 & 100
pp'-*Bisaminomethyldiphenylmethane* (II, *b*)	9·28 & 8·10 (M/160)	B (see Table I)	100 & 97

Von Braun (*Ber.*, 1937, **70**, 979) claimed to have produced (II, *a*) by the action of liquid ammonia on *pp'*-bisbromomethyldiphenyl; it is possible that his material was contaminated by secondary amines.

Note added in Proof.—Compounds (I, *c*—*f*) and (II, *a*—*f*) were kindly compared by Mr. L. G. Goodwin in experimental animal tests against *Trypanosoma rhodesiense*, *T. congolense*, *Plasmodium gallinaceum*, *Leishmania donovani*, and *Entamœba histolytica*. No activity was shown by any Type (II) compound. We are also grateful to Prof. S. D. Rubbo for testing the same series, *in vitro*, against *Cl. welchii*, *Strept. pyog.*, *Staph. aur.*, *B. coli*, and *B. Proteus*. Only (I, *d* and *e*) showed outstanding activity.

Thus, unless it can be shown that these organisms possess an enzyme specifically destroying Type (II) compounds, hypothesis (i) is no longer tenable.

EXPERIMENTAL.

[The microanalysis of bisaminomethyldiphenyl and its hydrochloride were carried out by one of us (J. A. M.); the remainder were done by Miss J. Fildes, who is hereby thanked.]

General.—The dinitrile (15 g.), Raney-nickel catalyst (*ca.* 5 ml. of sludge), and methanolic ammonia saturated at 0° (150 ml.) were placed in a chilled-steel hydrogenation bomb (unlined) with two ½ in. steel balls. These proportions allow about 7 mols. of ammonia, per cyano-group. Hydrogen was admitted at an initial pressure of 1300 lb./sq. in., and maintained at about 1200 lb. whilst the bomb was heated to 110° in 20 minutes with shaking. Uptake of hydrogen began at about 70°. It was rapid and approximately that required by theory. The autoclave was allowed to cool, and then chilled in ice. It was opened, and the contents filtered quickly with the assistance of some methanolic ammonia, in which the amines dissolve much better than in methanol. Carbon dioxide was excluded as much as possible from this and subsequent operations. The solvent was recovered by using a bath at 140° and applying a vacuum towards the end. The amines (crude yields about 90%) solidified on cooling and sometimes contained colloidal nickel hydroxide which caused foaming when the solids were distilled.

pp'-*Bisaminomethyldiphenyl* (II, *a*).—This was purified by distillation (b. p. 180°/0·5 mm.) and recrystallisation from 10 parts of toluene. The yield of pure material was 80%. A slightly under-

hydrogenated batch supersaturated badly. The substance is soluble in hot alcohol, benzene, and ethyl acetate, and in cold pyridine (Found: C, 79·5; H, 7·5; N, 13·3. Calc. for $C_{14}H_{16}N_2$: C, 79·2; H, 7·6; N, 13·2%). The compound and its derivatives had the following m. ps. (values of v. Braun, *loc. cit.*, in parenthesis): base, 144—145° (135°); picrate, 232—235° (decomp.) (222°); dibenzoyl derivative, 249—250° (243°); diacetyl derivative, 281—283° (272°). The *dihydrochloride* was formed by crystallisation from hot dilute hydrochloric acid. It is soluble in about 100 parts of cold water and readily precipitated by extra chloride ions (Found: C, 59·15; H, 6·3; Cl, 24·7. $C_{14}H_{18}N_2Cl_2$ requires C, 58·95; H, 6·4; Cl, 24·9%). The crystals developed a blue tint on exposure to sunlight.

pp′-*Bisaminomethyldiphenylmethane* (II, *b*).—This was purified by distillation at 0·5 mm., followed by dissolution in 5 parts of boiling benzene and treatment with 5 parts of light petroleum (b. p. 60—90°). The white crystals, m. p. 90° (80% yield), were dried in a vacuum over shredded paraffin. The *compound* is very soluble in alcohol without gradient, sparingly soluble in ether (Found: C, 79·4; H, 7·9; N, 12·2. $C_{15}H_{18}N_2$ requires C, 79·6; H, 8·0; N, 12·4%). The dihydrochloride (m. p. over 350°) is exceptional in this series in that it is difficult to precipitate with chloride ions; it is almost insoluble in alcohol and unaffected by light. The *dibenzoyl* derivative was prepared with benzoyl chloride in 10 volumes of pyridine (yield 90%) as white crystals from chlorobenzene, m. p. 224° (230° corr.), sparingly soluble in benzene, acetone, and alcohol (Found: N, 6·4. $C_{29}H_{26}O_2N_2$ requires N, 6·45%).

pp′-*Bisaminomethyldiphenyl ether* (II, *c*).—This was distilled (b. p. 186°/0·3 mm.), giving crystals (70% recovery) which began to melt at 56° and were completely molten at 77° (? double m. p.). The *product* was readily soluble in ethyl and amyl alcohols and in boiling toluene or acetone with gradient; only slightly soluble in ether and in light petroleum (Found: C, 73·0; H, 7·1; N, 12·2. $C_{14}H_{16}ON_2$ requires C, 73·6; H, 7·1; N, 12·3%). The dihydrochloride does not melt below 360°. The diacetate (m. p. 156°, anhydrous) was formed by dissolving the base in 8N-acetic acid at 50°, precipitating with acetone, and drying at 110°. It was readily soluble in cold water and hot ethanol.

1 : 3-(pp′-*Bisaminomethyldiphenoxy*)*propane* (II, *d*).—This was purified by distillation (b. p. 242°/0·5 mm.) and then recrystallised from alcohol, m. p. 90—91° (70° yield). It is sparingly soluble in boiling benzene; moderately so in boiling acetone. The dihydrochloride is sparingly soluble in cold water and readily soluble in hot water; it sinters at *ca.* 290° but does not melt below 360°. The *diacetate*, m. p. 178°, prepared as above, is readily soluble in cold water, moderately in boiling alcohol, and insoluble in acetone (Found: C, 62·0; H, 7·4; N, 6·85. $C_{17}H_{22}O_2N_2$, $2C_2H_4O_2$ requires C, 62·0; H, 7·4; N, 6·9%).

1 : 5-(pp′-*Bisaminomethyldiphenoxy*)*pentane* (II, *e*).—This was purified through the acetate without previous distillation. The base (70% yield), m. p. 74—75°, from aqueous ethanol, is readily soluble in pyridine and in methanol and has good gradients in toluene and chlorobenzene. It is very slightly soluble in ether and in light petroleum. The dihydrochloride is soluble in cold water and insoluble in ethanol and acetone. It sinters at *ca.* 270° but does not melt below 360°. The *diacetate*, m. p. 161°, is very soluble in water, moderately in cold and readily in boiling ethanol, and insoluble in acetone (Found: C, 63·4; H, 7·8; N, 6·4. $C_{19}H_{24}O_2N_2$,$2C_2H_4O_2$ requires C, 63·55; H, 7·9; N, 6·45%).

pp′-*Bisaminomethylstilbene* (II, *f*).—This *compound* was purified by recrystallisation first from chlorobenzene and then from ethanol, giving crystals, m. p. 210—211° (decomp.) on rapid heating (yield 75%). They are soluble in about 27 parts of boiling ethanol, moderately soluble in boiling benzene or pyridine (with gradient), and almost insoluble in acetone, ether, or light petroleum (Found: C, 80·6; H, 7·6; N, 11·7. $C_{16}H_{18}N_2$ requires C, 80·6; H, 7·6; N, 11·8%). The dihydrochloride is moderately soluble in boiling water (with gradient) and insoluble in alcohol or acetone. The diacetate, m. p. 206—207°, solidifies at 210° and melts again at 255° (approx.) and is readily soluble in water, slightly soluble in boiling alcohol, and insoluble in acetone.

trans-pp′-*Diaminostilbene*.—A three-neck flask (capacity 1 l.) was fitted with an efficient mechanical stirrer, a 24-in. water-cooled bulb condenser, and a cork containing a thermometer, the bulb of which was pushed down below the 250 ml. level. The operation was conducted under a good hood.

Sodium hydroxide sticks (125 g.) were broken into coarse grit and refluxed in the flask with methanol (500 ml.) until dissolved (about 90 minutes), heat being supplied by a glycerol-bath at 100°. The flame was extinguished, and the thermometer momentarily withdrawn while molten *p*-nitrotoluene (50 g.) was rapidly added. After 30 seconds a violent reaction set in, the temperature rising to 105° and falling back to 90° when the condensed methanol returned to the flask. The flask contents became deep red. The glycerol-bath was then heated for ½ hour to keep the flask contents at 100°. The thermometer was then withdrawn, and a condenser, arranged for distillation, inserted. Concentrated hydrochloric acid (1 equiv.; 300 ml. of 39% w/v) was added down the upright condenser during 15 minutes with rapid stirring. The bath was then maintained at 120° until 400 ml. of methanol, altogether, had been collected. The product consisted of a mixture of dinitrodibenzyl, dinitrostilbene, and (mainly) dinitrosostilbene. These substances were separated by Fischer and Hepp, but it was found more economical to reduce them together, *in situ*, taking advantage of the relative insolubility of diaminostilbene salts.

The temperature of the bath was lowered to 100°, and a solution of stannous chloride crystals (330 g.; 4 mols. per mol. of nitrotoluene) in concentrated hydrochloric acid (330 ml.), warmed to 80°, was added down the upright condenser during 15 minutes. Stirring and heating at 100° (bath temp.) were continued for 2 hours. The flask was then cooled and kept in ice for 2 days.

The precipitate of sodium chloride and diaminostilbene stannichloride was filtered off, pressed well, and extracted successively with 500, 200, and 50 ml. of boiling water, leaving about 1 g. of sludge. The combined filtrates were boiled and treated with sodium hydroxide (*ca.* 350 ml. of 5N) until Orange-II paper was reddened. The mixture was heated for ½ hour on the boiling water-bath and again adjusted to redden Orange-II. The precipitate was filtered hot, pressed, and washed until the filtrate ceased to redden phenolphthalein. The cake was dissolved in the minimum (*ca.* 300 ml.) of boiling N-hydrochloric acid, 75 ml. of 10N-hydrochloric acid were then added, and the whole refrigerated overnight. Next day the diaminostilbene hydrochloride was filtered off, dissolved in boiling water (150 ml.) containing 10N-hydrochloric acid (1 ml.), and treated with sodium hydroxide, as above. The cake was collected, pressed hard, washed well, and dried at 120°. The yield was 17·0 g. (45%) of orange powder, m. p. 214°.

This was purified by boiling with 20 parts of chlorobenzene, filtering hot, and cooling in ice for a day (85% recovery; m. p. 225—226°).

Finally, recrystallisation from dilute alcohol removed a trace of orange impurity and gave minute, almost colourless crystals, m. p. 227—228° equal to the highest uncorrected m. p.s in the literature (Calvin and Buckles, *J. Amer. Chem. Soc.*, 1940, **62**, 3324; Klinge, *Ber.*, 1883, **16**, 943).

The authors wish to thank Professors J. C. Earl and A. K. Macbeth for their interest in this work, and Dr. A. J. Ewins for supplying the dinitriles. This work was supported by the National Health and Medical Research Council, the Commonwealth Research Fund, and the Wellcome Foundation.

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276. *The Crystal Structure of Ammonium Nitrate III, and Atomic Scattering Factors in Ionic Crystals.*

By T. H. GOODWIN and J. WHETSTONE.

The crystal structure of ammonium nitrate III has been redetermined in the light of revised optical and *X*-ray evidence.

IN the course of an investigation into the conditions of stability of ammonium nitrate III, the form normally stable from 32·3° to 84·2°, we measured the series of single-crystal rotation and oscillation photographs which we obtained, and compared our data with those of Hendricks, Posnjak, and Kracek (*J. Amer. Chem. Soc.*, 1932, **54**, 2776). Although there is general agreement between their observations and ours, there are certain marked discrepancies [see information in Tables II and III concerning the planes (002) and (004), (101), and (200)]. Moreover, there are frequently wide discrepancies between their observed and calculated intensities, as, for example, for the planes observed to have " moderate " intensities.

We are unable to account for the observational discrepancies, but for the rest, it seems possible that the authors were aware of the optical data which Hendricks, Deming, and Jefferson published later (*Z. Krist.*, 1933, **85**, 145) and, believing them to be correct, proposed a structure in conformation with them. They say that their agreement between observed and calculated intensities is only moderate. A difficulty in trying to explain these discrepancies is that although the authors state that the interfacial angles between the needle zone faces is 90° 0′ (faces therefore *a* {100} and *b* {010}) they quote no data derived directly from rotation, oscillation, or Weissenberg photographs about the *a*- or *b*-axes apart from the intensities of {001} which we consider erroneous and for which they fail to record calculated intensities. We therefore decided to redetermine the structure.

Since ammonium nitrate III is stable only above 32°, all manipulations of the crystals had to be carried out above this temperature. The specimens used were grown from aqueous-alcoholic solution in a thermostatic hot-air chamber at 50°, and selected and mounted while still in the chamber. They were then rapidly transferred to the goniometer arcs while a stream of hot air at *ca.* 42° was allowed to flow over crystal and arcs alike. Optical goniometry revealed that the crystals, which were long needles, usually had only the four prism faces of the {110} form present, the angle (110);(1$\bar{1}$0) being 94°. There is probably no significance in this difference of habit between our crystals and those of Hendricks *et al.*

After the camera had been placed in position, hot air was introduced into it by a wide tube inserted through the lid and reaching down to near the level of the crystal, a thermometer being present in the air stream to ensure maintenance of a sufficiently high temperature (*ca.* 42°). The *X*-radiation employed was from the copper target of a Shearer tube with a nickel-foil filter. The following axes were measured: $a = 7{\cdot}14$, $b = 7{\cdot}65$, $c = 5{\cdot}83$ A. These compare satisfactorily with the results of Hendricks *et al.*, *viz.*, $a = 7{\cdot}06$, $b = 7{\cdot}66$, $c = 5{\cdot}80$ A. Examination of oscillation photographs about the *a*, *b*, and *c* axes revealed {0*kl*} present only when *k* is even, {*h*0*l*} present only when $h + l$ is even, {*hk*0} and {*hkl*} present in all orders. These extinctions are consistent with the space-group *Pbnm* (V_h^{16}) assumed by the American investigators although *Pbn* (C_{2v}^2) is also possible. For preliminary calculations the space-group of higher symmetry *Pbnm* was assumed.

The structure factors for planes of the {*hk*0} zone are the same for both space-groups and, as is shown later, the atomic positions were deduced by constructing a Fourier projection on (001). Since it was impossible to carry out work with heated crystals on the Weissenberg

instrument available, visual estimates of intensities had to be made from rotation and oscillation photographs, with consequent limitations of accuracy. It was found possible, using the atomic positions definitely located by the Fourier synthesis, to postulate a structure based on the symmetry elements of *Pbnm*, giving satisfactory agreement between observed and calculated intensities within the limits of accuracy of the work. In addition, the packing of the atoms in the unit cell is such that there is little possibility of changes in the relative positions indicated if on the one hand the projection on (001) is to be maintained while on the other the space-group is to be altered to *Pbn*; any such changes would increase the range of $NH_4 \ldots . O$ distances observed on the structure. Thus we consider that the choice of the space-group of higher symmetry, *Pbnm*, is justified.

In this space-group, then, eight asymmetric units are required, four being mirror images of the others, but as only four NH_4NO_3 units, *i.e.*, four NH_4^+ and four NO_3^- ions, are present, these must possess two-fold symmetry; since the space-group does not involve axes of rotation, the ions are restricted to central or planar symmetry. Both these types need to be considered for, though neither the tetrahedral NH_4^+ nor the planar NO_3^- group can have a centre of inversion when " at rest ", in ammonium nitrate I, the form stable from 125° to the melting point at 169·5°, there is only one ion of each species in a cubic cell and therefore each must be rotating in a way which enables it to simulate cubic symmetry. In ammonium nitrate III rotation of the NH_4^+ and NO_3' could confer on them pseudo-central symmetry. On the other hand, (*a*) the latter modification is stable at considerably lower temperatures and its ions are therefore less likely to be rotating in the solid state, and (*b*) the number of ions present is the minimum required if they are planar and at rest. We decided, therefore, to begin by placing the nitrate ions on the symmetry planes, but in view of the fact that the ammonium ions are more nearly spherical and therefore more readily capable of free rotation, we decided to consider their location at centres of inversion and on planes of symmetry in turn. In the latter case the co-ordinates of the ammoniacal nitrogen are :

$$(a)\ u_A, v_A, \tfrac{1}{4};\ u_A, \bar{v}_A, \tfrac{3}{4};\ \tfrac{1}{2} - u_A, \tfrac{1}{2} + v_A, \tfrac{1}{4};\ \tfrac{1}{2} + u_A, \tfrac{1}{2} - v_A, \tfrac{3}{4}.$$

In the former they may be either :

$$(b)\ 0,0,0;\ 0,0,\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2},\ \text{or}\ \ (c)\ \tfrac{1}{2},0,0;\ \tfrac{1}{2},0,\tfrac{1}{2};\ 0,\tfrac{1}{2},0;\ 0,\tfrac{1}{2},\tfrac{1}{2}.$$

For the nitrate ions two dispositions on the symmetry planes of the crystal are possible, *viz.*, so that all four atoms of each ion are on the (same) symmetry plane or so that the nitrogen and one oxygen are on the plane, the other oxygens being above and below this. In the first case pronounced negative optical birefringence would occur, the minimum refractive index α being perpendicular to the symmetry planes, *i.e.*, parallel to the *c*-axis (cf. potassium nitrate and aragonite; Bragg, " Atomic Structure of Minerals ", Oxford Univ. Press, 1937, pp. 119 *et seq.*). In the second, γ, the greatest refractive index, would be parallel to *c*. In fact, γ is parallel to *c*, so that the second possibility is the correct one; since the optic axial angle is high ($2V \approx 90°$) it follows that the plane of the ion must be quite oblique to both the *a* and the *b* axis.

The atomic co-ordinates of N and one O of the NO_3^- must therefore be as in (*a*) above but with parameters u_N, v_N and u_O, v_O. The other oxygens are in general (*i.e.*, eight-fold) positions :

$$(d)\ x,y,z;\ \bar{x},\bar{y},\tfrac{1}{2}+z;\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{2}-z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\bar{z};$$
$$x,y,\tfrac{1}{2}-z;\ \bar{x},\bar{y},\bar{z};\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{1}{2}+z.$$

To locate the various atoms, we first considered the orders of (001) since they involve only the *z*-co-ordinates. For those the structure factor F_{00l} is :

$$F_{00l} = 8f(O)\cos 2\pi lz + 4f(O)\cos 2\pi\frac{l}{4} + 4f(N)\cos 2\pi\frac{l}{4} + 4f(A)\cos 2\pi\frac{l}{4},$$

or

$$F_{00l} = 8f(O)\cos 2\pi lz + 4f(O)\cos 2\pi\frac{l}{4} + 4f(N)\cos 2\pi\frac{l}{4} + 4f(A)\cos 2\pi\frac{l}{2}$$

according as the ammonium ion is situated on the symmetry plane or at a symmetry centre; f(O), f(N) and f(A) are the atomic scattering factors of oxygen, nitrate nitrogen, and ammonium respectively. Hendricks, Posnjak, and Kracek " assumed that f(A) for Cu-*K* radiation is

approximately the same as determined for Mo-K radiation diffracted from NH_4Cl (Wyckoff and Armstrong, *Z. Krist.*, **1929, 72, 319**), that f(O) is the same as for oxygen in nickel oxide (Cu-K radiation) (Wyckoff, *Physical Rev.*, **1930, 35, 583**; " Structure of Crystals ", 2nd Edn., 1931, p. 100), and that $f(N) = 0{\cdot}35\ f(O)$ independent of $\sin\theta/\lambda$ ". It is thus implied that, so far as the diffraction of X-rays is concerned, the nitrate ion approximates to a N^{5+} ion surrounded by three O^{2-} ions. In view of the completed L shells of nitrogen and oxygen in nitrate ions as formulated by chemists, we have preferred to regard the f values of these atoms as the same, with $f_0(N) = f_0(O) = 8$, f_0 being the value of f when $\theta = 0$. Of the various theoretical arguments in support of this view, we quote only two. It is well known that the polarising power of a cation increases with increasing charge and decreasing radius. Since the " radii " of N^{5+} and, say, Li^+ are quoted by, *e.g.*, Pauling (" Nature of the Chemical Bond ", 2nd Edn., p. 346) as 0·11 and 0·60 A., respectively, it follows that the polarising power of the N^{5+} will be so great as to lead to N–O bonds which are essentially covalent. Secondly, the uniformity of structure of the nitrate ion as a planar equilateral triangle in which the central nitrogen has no tendency to be surrounded by more than three oxygens or other " anions ", shows that the N–O bonds are directed in space and therefore are covalent, not electrovalent.

Using, then, these atomic scattering factors, we found that if the NH_4^+ ion is on the mirror plane z must have a value of between 0·06 and 0·07 in order to account for the observed relative intensities of (002), (004) and (006); z was selected as 0·06, equivalent to a distance of about 2·21 A. for O . . . . O in the nitrate ion, or 1·27 A. for N . . . .O, which latter value lies between the measurement of 1·21 A. made by Elliott (*J. Amer. Chem. Soc.*, **1937, 59, 1380**) for the nitrate ion in sodium nitrate, and the value of 1·31 A. calculated by Pauling on the basis of one double bond resonating between the three positions. If the ammonium ion was placed at a symmetry centre no such satisfactory relative intensities could be calculated.

We next drew, on scaled diagrams of the (001) plane, the traces of various particularly strong and particularly weak $\{hk0\}$ planes (excluding space-group halvings). On examining the resulting diagram with the assistance of a scale model of the nitrate ion (edge = O . . . . O proportional to 2·21 A.), arranged so that one O . . . . O direction was perpendicular to the diagram, tentative positions for the atoms of this ion were obtained which permitted a reasonable location of the NH_4^+ ion on the symmetry plane. From these we calculated, after some slight adjustments, structure factors which were in approximate agreement with our qualitative estimates of intensity. In an endeavour to refine the structure we then made by visual estimation numerical assays of the intensities of as many as possible of the $\{hk0\}$ planes from rotation and oscillation photographs and constructed a Fourier projection on (001).

This projection proved far from satisfactory because, while indicating unequivocally the two oxygens in the general positions (d), it left considerable doubt as to the placing of the ammonium ion and the third oxygen on the reflection planes. One of these was revealed as a definite peak in the landscape but the other only as an upland region. According to whether and where the ammonium or oxygen is placed in this upland region three alternative structures are obtained which give F values for the $\{hk0\}$ planes of roughly the same magnitude as those estimated visually. However, by trial and error methods the ammonium ion was eventually placed in this region in a position which led to satisfactory agreement with the intensities of reflections over all three principal zones as well as for the $\{hkl\}$ planes. The nitrate nitrogen was suitably located on the line joining the " special " and " general " oxygens in the projection. In view of the large changes in structure amplitude brought about in certain planes by movements of the atoms of less than one-hundredth of the cell edge, and the impossibility of testing all the combinations of atomic positions within the tolerances allowed by the Fourier synthesis, the agreement between observed and calculated intensities is as good as can be expected.

TABLE I.

Atomic co-ordinates.

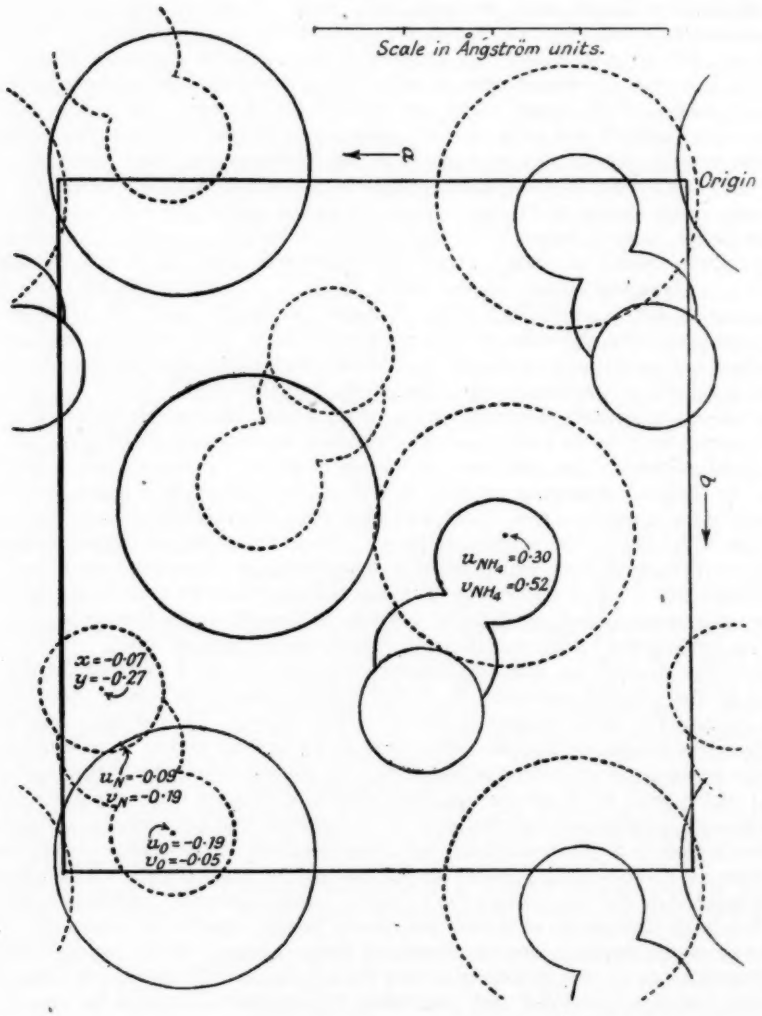
x	= 0·05—*0·06*	y	= 0·17—*0·175*—0·18	z	= *0·06*—0·07
u_N	= 0·13—*0·14*	v_N	= 0·14—*0·145*—0·15	w_N	= *0·25*
u_O	= *0·30*—0·29	v_O	= 0·08—*0·085*—0·09	w_O	= *0·25*
u_{NH_4}	= 0·30—*0·32*	v_{NH_4}	= *−0·02* to −0·03	w_{NH_4}	= *−0·25*

Table I gives the limits within which we consider the parameters of the various atoms to lie, the figures in italics being those used in calculating the structure factors and intensities of Tables II, III, and IV.

Since the crystals were thin needles of nearly square cross-section, it was considered unnecessary to apply absorption corrections to the observed intensities of the {*hk*0} planes. They have, however, been applied to those of the other prism zones, though not to the {*hkl*} planes, calculations of which were made rather as a final check.

In Table II are given first the observed intensities of the planes of the {*hk*0} zone. Then in col. 3 are recorded the structure factors calculated from the final ionic model, the four atoms

FIG. 1.

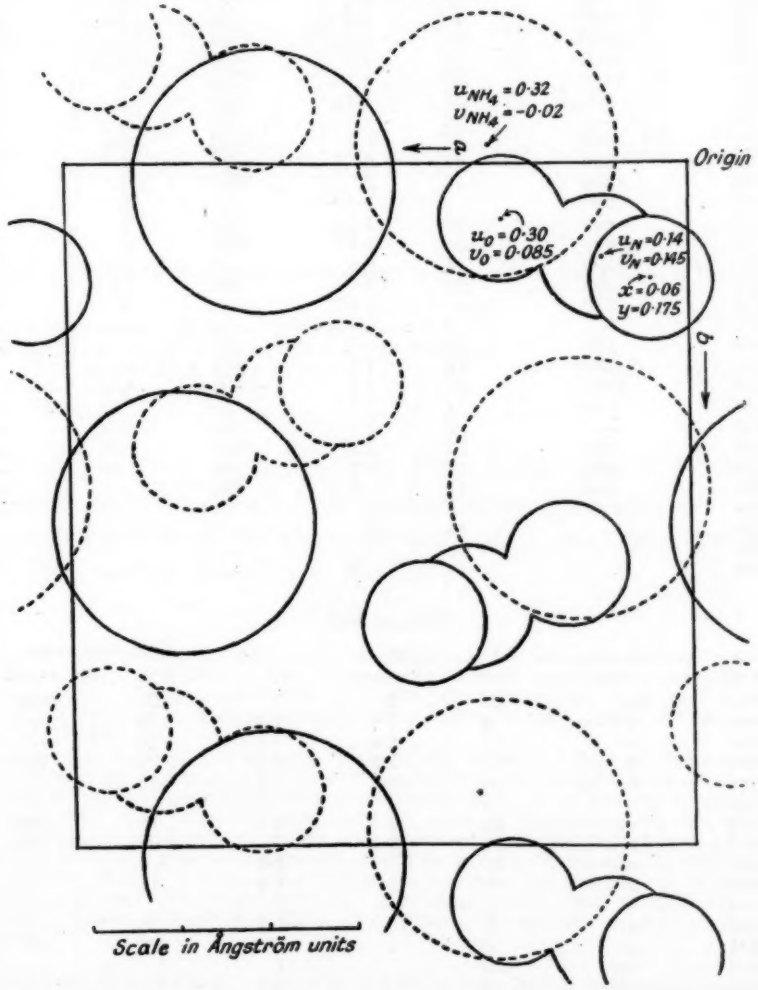


of the nitrate ion all being supposed to have the same atomic scattering factors with $f_0(O) = f_0(N) = 8$. Col. 4 gives the factor $L = (1 + \cos^2 2\theta) \sin 2\theta$ by which F^2 is converted into the intensity I, recorded in col. 5. Cols. 6 and 7 record the intensities observed and calculated by Hendricks *et al.* Table III contains the absorption corrections where applied; these were calculated from the lengths of the paths of the *X*-ray beam through the crystals and the mass absorption coefficients recorded in the " International Tables for the Determination of Crystal Structures," 1933, Vol. II, p. 577. Apart from this, Tables III and IV will be readily understood by comparison with Table II.

It will be seen that our observed and calculated results are in better agreement than those of Hendricks, Posnjak, and Kracek. The principle difference between the two structures is in the disposition of the nitrate ions, which in our model (Fig. 1) are more nearly parallel to the

a- than to the *b*-axis, the converse being the case with the structure reported by the Americans (Fig. 2). Our proposal would therefore lead to refractive indices $\alpha//b$, $\beta//a$, $\gamma//c$ The measured values as recorded by Hendricks, Deming, and Jefferson (*Z. Krist.*, **1933, 85**, 145) are $\alpha = 1{\cdot}463//a$, $\beta = 1{\cdot}543//b$, and $\gamma = 1{\cdot}600//c$. Our own measurements, carried out on mounted crystals of known orientation (as determined by *X*-rays) agree with these numerically, but we find $a//b$ and $\beta//a$. In view of the fact that the crystals are long needles with their needle zone

FIG 2.



FIGS. 1 and 2.—*Fig.* 1 *represents the unit cell of ammonium nitrate III deduced in this investigation, projected parallel to the* c*-axis ; Fig.* 2 *is a similar projection of the structure of Hendricks, Posnjak, and Kracek. The unbroken and the dotted circles represent atoms located on or about reflection planes at* $c = \frac{1}{4}$ *and* $\frac{3}{4}$*, respectively. The large circles represent ammonium ions (Pauling's radius* 1·48 A.*), while the groups of small circles represent the nitrate ions, and oxygens in the general positions being superimposed one on another in the projection. The radii of oxygen and nitrogen are taken as Pauling's covalent radii (*0·66 A. *and* 0·70 A.*, respectively).*

faces at or nearly at right angles, it is not surprising that the vibration directions of the fast and medium rays should have been wrongly identified. Thus the revised optical properties support our proposed ionic arrangement. In our structure the NH_4^+ ions are distant 2·7—3·2 A. from their nearest oxygen neighbours, while in theirs the mean of nine such distances ranging from 2·75 to 3·13 A. is 2·95 A.

TABLE II.

	Intensity, obs,			Intensity: G. & W.,	Intensity: H., P., & K.,	
*hk*0.	num.	F, calc.	*L*.	calc.	obs.	calc.
200	500	−10	4·5	450	vw	8
400	130	−12	1·7	250	vw	8
600	—	−10	1	100	vw	—
020	0—30	7	4	200	vw	1
040	1300	−14	2	400	m	660
060	800	30	1	900	w	—
110	1000	15	6·5	1450	m	550
210	8000	−44	3·75	7000	vvs	3000
310	2600	38	2·5	3600	mms	10
410	1800	−35	1·7	1750	s	400
510	800	−31	1·25	1200	m	—
610	—	− 3	1	10	—	—
120	5000	−45	4	8000	ms	370
220	10,000	−44	3	6000	s	500
320	1300	−28	2	1600	m	90
420	260	1	1·5	—	w	50
520	400	−15	1·25	250	w	—
130	10,000	−60	2·75	9900	s	270
230	500	4	2·2	40	mw	140
330	500	20	1·7	700	vw	80
430	130	—	1·35	—	w	—
530	—	3	—	10	—	—
140	250	14	1·8	350	a	200
240	130	10	1·7	170	a	15
340	2300	31	1·4	1300	mms	—
440	130	4	1·1	20	—	—
540	—	8	1	64	—	—
150	800	15	1·5	350	—	—
250	260	21	1·3	500	—	—
350	500	14	1·2	270	—	—
450	—	− 3	1	10	—	—
160	—	15	—	—	—	—
260	—	10	—	—	—	—
360	—	− 5	—	—	—	—

TABLE III.

*h*0*l* or 0*k*.	Intensity, obs.	F, calc.	Abs., corr.	*L*.	Intensity, calc. G. & W.	Intensity, calc. H., P., & K.
101	ms	22	2	5	1125	4000
103	vw—a	4	1·8	1·8	16	—
105	w	11	2·2	1·0	50	—
202	s	58	2·3	2·45	4000	750
204	m	24	2·3	1·2	310	—
206	w	8	?	1·2	?	—
301	vw	14	12·5	2·4	40	200
303	mw	21	3·3	1·5	200	160
305	vw	16	?	1·0	?	—
402	a	10	10	1·4	14	3
404	a	8	?	1	?	—
406	a	7	10	1·2	5	—
501	w	8	3	1·2	25	—
503	vw	20	?	1	?	—
505	vw	6	?	1·5	?	—
002	s	37	—	3·4	4630	—
004	m	31	—	1·3	1250	—
006	w	23	—	1·1	580	—
021	s	54	3·3	3·7	4000	70
023	vw	11	2·1	1·7	90	—
025	mw	32	?	1	?	—
022	s	54	2·1	2·5	3450	1250
024	mw	23	2·1	1·2	300	—
026	a	9	?	1·1	?	—
041	a	6	4·5	1·8	15	20
043	mw	35	4	1·25	375	10
045	a	4	?	1·1	?	—
042	a	8	4	1·4	20	2
044	a	1	4	1	0	—
046	a	3	?	1·7	?	—

TABLE IV.

hkl.	*I*, obs.	F, calc.	*L.*	*I*, calc. G. & W.	*I*, calc. H., P., & K.	*hkl.*	*I*, obs.	F, calc.	*L.*	*I*, calc. G. & W.	*I*, calc. H., P., & K.
111	s	23	4·7	2500	1300	151	w	22	—	—	—
211	s	32	3·5	3500	15	251	w	20	1·2	480	—
311	vw	3·5	2	20	0	112	s	23	2·9	1550	400
411	w	8	1·5	100	7	212	vw	5	2·4	60	80
511	w	13	1·2	200	—	312	mw	20	1·7	680	280
121	ms	25	3·5	2200	240	412	mw	17	1·3	380	140
221	w	8	2·6	170	30	122	m	16	2·4	700	280
321	mw	7	1·9	100	130	222	mw	11	2	250	65
421	a	9	1·4	110	2	322	mw	16	1·5	380	15
521	vw	8	1·1	70	—	422	w	3	1·4	13	3
131	mw	8	2·4	150	100	132	a	3	1·8	16	10
231	w	5	2	50	5	232	w	7	1·6	80	100
331	vw	10	1·6	160	37	332	ms	34	1·4	1500	0
431	mw	23	1·3	650	—	432	vw	6	1·1	40	—
141	m—ms	40	1·7	2700	4						
241	m	23	1·5	750	70						
341	a	5	1·35	30	—						
441	w	6	1·1	40	—						

In conclusion, we wish to express our gratitude to Professor J. M. Robertson, F.R.S., for his interest in this work.

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277. *The Separation of* d-*Fructose from Other Natural Sugars as its* 2 : 3-4 : 5-*Diacetone and* 1 : 2-*Monoacetone Derivatives : Observations on the Behaviour of Acetone Derivatives of Monosaccharides towards Cold Decinormal Sulphuric Acid.*

By D. J. BELL.

A simple procedure is described for the isolation of *d*-fructose from mixtures of monosaccharides as the 2 : 3-4 : 5-diacetone derivative. Glucose, mannose, xylose, and rhamnose do not interfere. The method is not applicable where galactose, arabinose, or fucose are present in quantity; in such instances a procedure leading to the isolation of 1 : 2-monoacetone fructose is adopted.

The diacetone derivatives of glucose, mannose, and xylose and the monoacetone derivatives of rhamnose and ribose (all understood to be derived from the furanose form of the sugars) are hydrolysed to the corresponding monoacetone compounds, or to the free sugar, by several hours' treatment with 0·1N-sulphuric acid at room temperature. On the other hand, 2 : 3-4 : 5-diacetone fructose, and the diacetone derivatives of galactose, fucose, and arabinose (all believed to have pyranose structures) resist this hydrolytic attack. 1 : 2-4 : 5-Diacetone fructose is anomalous : it behaves as if it had a furanose ring although it is generally considered to be derived from fructopyranose. Use being made of this difference in hydrolytic behaviour, a number of sugar separations are facilitated through their readily obtained acetone derivatives.

THE identification of *d*-fructose, especially in crude material of biological origin, has always presented difficulty. The only crystalline derivative hitherto employed to this end is the phenylmethylosazone (Neuberg, *Ber.*, 1902, **35**, 960; Neuberg and Mandl, *Arch. Biochem.*, 1946, **11**, 451). This substance is formed in variable yield; when it is isolated from mixtures its physical properties tend to be erratic, and in theory, if not in practice, it may also be formed from *d*-glucose and *d*-mannose. It is also necessary to work in relatively concentrated solutions, so the presence of large amounts of mineral matter, etc., besides other sugars, as often occur in biological extracts, complicates, or may even render impossible, isolation of the phenylmethylosazone. Work in this laboratory demanded an unequivocal means of identifying relatively small amounts (*e.g.*, 100 mg.) of *d*-fructose under conditions such as those described.

It was considered that treatment of the dried material with acetone and a suitable catalyst would provide a convenient means of separating carbohydrates (as monosaccharides) from inert material and at the same time produce derivatives which, directly or indirectly, would

lead to characterisation of the sugars, and this has proved to be the case. Irvine and Garrett (*J.*, 1910, **97**, 1283) observed that 2 : 3-4 : 5-diacetone fructose (the so-called " β "-derivative) displayed remarkable stability towards cold dilute acid, in marked contrast to the behaviour of the 1 : 2-4 : 5-isomer (" α " diacetone fructose). Ohle and Koller (*Ber.*, 1924, **57**, 1566) confirmed this finding and further noted that 1 : 2-5 : 6-diacetone glucose was, like α-diacetone fructose, unstable to cold 0·1N-sulphuric acid, both substances losing at least one *iso*propylidene radical by hydrolysis. Ohle and Koller further demonstrated that, although low concentration of mineral acid catalyst favoured the formation of α-diacetone fructose (cf. E. Fischer, *Ber.*, 1895, **28**, 1164; Irvine and Garrett, *loc. cit.*; Montgomery, *J. Amer. Chem. Soc.*, 1934, **56**, 419), yet increase in concentration of the catalyst led to increasing formation of the β-isomer, resulting in a series of mixed products, until, at a concentration of 4% of sulphuric acid, pure β-diacetone fructose was formed. The use of catalysts such as zinc chloride (H. O. L. Fischer and Taube, *Ber.*, 1927, **60**, 485) favours formation of the α-derivative.

In the present work the above observations have been confirmed and extended. The presence of 5% (v/v) of sulphuric acid in the acetone condensation (optimum duration, 6 hours) produces over 70% of the theoretical yield of β-diacetone fructose while diacetone glucose, under similar conditions, is formed to the extent of 50—55%. If a mixture of glucose and fructose, or sucrose itself, is treated in the above manner, the products are mainly β-diacetone fructose and diacetone glucose along with minor quantities of monoacetone derivatives. Partition of this mixture between chloroform and water leaves the " mono "-constituents in the aqueous phase. Six hours' treatment of the material obtained from the chloroform phase with 0·1N-sulphuric acid effects hydrolysis of the diacetone glucose and the α-diacetone fructose to the monoacetone derivatives; pure β-diacetone fructose is obtained by partition into chloroform. If all the " mono "-residues are brought into the dry state, recondensed with acetone, treated with dilute acid, and partitioned as before, the total yield of β-diacetone fructose may approach 80% of the theoretical.

It having been established that fructose could satisfactorily be separated from glucose, it seemed desirable to determine whether differences in hydrolytic behaviour existed among the acetone derivatives of other natural monosaccharides, and to what extent their presence might interfere with the isolation of β-diacetone fructose. The required derivatives were prepared under the conditions described above (which are not necessarily optimum for sugars other than fructose). Those compounds which are considered to be derived from the pyranose form of the parent sugar, *viz.*, the diacetone derivatives of *d*-galactose, *l*-arabinose, and *l*-fucose, all proved completely resistant to the action, for 6 hours, of 0·1N-sulphuric acid. In contrast, the furanose compounds, diacetone *d*-mannose, diacetone *d*-xylose, and monoacetone *l*-rhamnose, behaved similarly to diacetone glucose and were converted into substances which could not be extracted from water by chloroform. Crude " monoacetone *d*-ribose " (see Experimental) is hydrolysed comparatively slowly, but, although it is partitioned into chloroform, the restricted occurrence of the parent sugar is unlikely to cause difficulties. It was found practicable to isolate β-diacetone fructose from a mixture composed of 200 mg. each of *d*-fructose and six other sugars, despite the presence of both diacetone *d*-galactose and diacetone *l*-arabinose in the final product of the chloroform–water partition.

A possible explanation of the marked difference in stability towards acid exhibited by the two types of diacetone sugar may lie in the fact that in each example possessing a furanose sugar ring the labile *iso*propylidene radical is united through a primary alcoholic group. However, in the instance of the labile radical of α-diacetone fructose, if we assume that the hitherto accepted pyranose structure is correct, two secondary *cis*-alcoholic groups (4 and 5) are engaged. Such configurations are stable when the sugar ring is pyranose, and labile when it is furanose. The 1 : 2-monoacetone fructose derived from α-diacetone fructose is well known to possess a pyranose structure. It may be possible that α-diacetone fructose is really a derivative of fructofuranose having its *iso*propylidene radicals attached through positions 1 : 2 and 4 : 6, and that hydrolysis to the monoacetone derivative is accompanied by enlargement of the ring. Our present knowledge of the chemistry of the ketoses is too scanty definitely to forbid such a transformation.

If it is desired to separate fructose from sugars which form pyranose derivatives, with acetone, condensation catalysed by 0·3% (v/v) of sulphuric acid will lead to the production of α-diacetone fructose. The action of dilute acid will hydrolyse the latter to 1 : 2-monoacetone fructose which can be partitioned from chloroform into water, leaving the pyranose diacetone compounds in the organic solvent. The yield of monoacetone fructose thus obtained is good.

Experimental.

Evaporation of solvents was conducted below 50°, under diminished pressure. M. p's. are uncorrected. Measurements of optical activity were made in a 2-dm. tube. Acetone was kept, for at least 2 weeks, over calcium chloride before use.

α-Diacetone d-*Fructose.*—(a) *Catalyst, zinc chloride.* The method of H. O. L. Fischer and Taube (*loc. cit.*) was followed. From 2 g. of fructose, the yield (not improved by using varying amounts of catalyst) was 3·8 g., after recrystallisation from ligroin (b. p. 60—80°); m. p., 119°, $[\alpha]_D^{16°}$ (water) — 161·0°; (chloroform) — 147·3°.

(b) *Catalyst, 0·3% sulphuric acid.* 5 G. of fructose were shaken with 50 ml. of dry acetone containing 0·15 ml. of concentrated sulphuric acid; after 24 hours the sugar was completely dissolved. The reaction mixture was kept for a further 24 hours, stirred with anhydrous sodium carbonate to remove acid, filtered, and evaporated. The residue was dissolved in water, the pH adjusted to 8·5—9 by addition of dilute sodium hydroxide, and the solution distilled under reduced pressure to remove mesityl oxide. The solution was then shaken with a little charcoal, filtered, and three times extracted with its own volume of chloroform. On evaporation of the dried (Na_2SO_4) extract, 5·29 g. of crystalline material were left. Recrystallised from ligroin (b. p. 60—80°), 4·79 g. (66%) of pure α-diacetone fructose were obtained, having m. p. 119°, $[\alpha]_D^{16°}$ (chloroform) — 147·3°.

β-Diacetone Fructose.—(a) *Catalyst, 4% sulphuric acid* (cf. Ohle and Koller, *loc. cit.*). 5 G. of fructose were shaken with 50 ml. of dry acetone containing 2 ml. of sulphuric acid. The sugar dissolved rapidly and, after being kept for 3 hours, the solution was worked up in the manner described for the α-isomer. The crude product (3·7 g.) was crystalline; it proved, however, to consist of mixed crystals of the α- and the β-isomer which could not be separated by fractional crystallisation; m. p. *ca.* 80°, $[\alpha]_D^{16°}$ (water) — 62·8°. (Ohle and Koller observed similar inseparable mixtures when using lower concentrations of catalyst.) This mixture corresponds to one of 25% "α" with 75% "β"; 3·2 g. were kept for 3 hours in 0·1N-sulphuric acid solution. After neutralisation of the acid with dilute sodium hydroxide, the solution was three times extracted with its own volume of chloroform. On evaporation of the solvent, 2·4 g. (75% of the mixed crystals taken) of needles, m. p. 93—94°, remained. After recrystallisation from ligroin (b. p. 60—80°), the m. p. rose to 95—96° and $[\alpha]_D^{16°}$ (water) was — 33·1° (*c*, 7); these constants agree with those previously recorded.

(b) *Catalyst, 5% sulphuric acid.* 2·5 G. of fructose were shaken for 4 hours with 25 ml. of acetone containing 1·25 ml. of sulphuric acid, and the mixture treated as before. The chloroform phase yielded 2·7 g. (74%) of crystals, m. p. 90°, $[\sigma]_D^{16°}$ (water) —41·9°, corresponding to a mixture of 93% "α" with 7% "β".

The aqueous phase from the chloroform extraction was evaporated to dryness, and 0·5 g. of a colourless solid obtained; this was treated with 10 ml. of acetone (5% H_2SO_4) in the manner described above for 4 hours. After the customary separation by partition, 0·4 g. of crystalline diacetone fructoses was obtained, bringing the total yield to 3·1 g. 2·5 G. of this material were subjected to the action of 0·1N-sulphuric acid for 2 hours; the yield of pure β-diacetone fructose (m. p. 95—96°) was 2·3 g. (*ca.* 79%).

Ohle and Koller stated that the specific rotation (in water) of β-diacetone fructose varies with the concentration of the solute. That this is not the case is shown by the following observations:

Concn., g./100 ml.	7·0	3·5	1·0
$[\alpha]_D^{16°}$	−33·1°	−33·1°	−32·95°

The specific rotation in chloroform was also found to be — 24·8° over a range of concentrations.

The Stability of β-Diacetone Fructose towards 0·1N-Sulphuric Acid.—352 Mg. of pure β-diacetone fructose were dissolved in the acid, and the solution kept at room temperature for 6 hours. After the pH of the solution had been brought to about 9 by addition of sodium hydroxide, it was three times extracted with chloroform. Evaporation of the chloroform phase yielded 350 mg. (99·5%) of crystals, m. p. 95°, $[\alpha]_D^{16°}$ (water) — 32·9° (*c*, 2·5).

Conversion of α- into β-Diacetone Fructose.—1·300 G. of α-diacetone fructose were dissolved in 20 ml. of acetone containing 1 ml. of sulphuric acid. After being kept for 6 hours at room temperature, the product was isolated by the usual procedure. The yield of crystals was 1·202 g. (92·5%); $[\alpha]_D^{16°}$ was — 32·7° (chloroform), corresponding to a mixture of 90% "β" with 10% "α". The material was therefore treated with 0·1N-sulphuric acid for 6 hours, and the β-diacetone fructose isolated by partition into chloroform. 1·010 G. of needles were obtained, corresponding to 93·5% of the β-diacetone compound estimated to be present in the product of the acetone treatment. The material had $[\alpha]_D^{16°}$ (chloroform) — 24·8° (*c*, 5·78), and after recrystallisation from ligroin (b. p. 60—80°) melted at 95—96°.

Action of Acetone containing 5% of Sulphuric Acid on Some Monosaccharides.—The finely powdered sugar was shaken for 6 hours (unless stated to the contrary) with 20 parts (v/w) of acetone containing 5% (v/v) of the catalyst. The reaction mixture was treated as in the preparation of α-diacetone fructose, and the product isolated by triple chloroform extraction from water.

(*a*) *d*-Glucose (5 g.). Crude yield (crystalline) 4·59 g. (63%); recrystallised from ligroin (b. p. 60—80°), 3·84 g. (53%), m. p. 110°; $[\alpha]_D^{16°}$ (chloroform) — 12·3° (*c*, 5·6).

(*b*) *d*-Galactose (5 g.). After 24 hours, 0·9 g. of sugar remained undissolved; yield (syrup) 3·55 g. (60%); $[\alpha]_D^{16°}$ (chloroform) — 55·0° (*c*, 2·14), (water) — 42·8° (*c*, 2·77).

(*c*) *d*-Mannose (2 g.). 1·802 G. of crystals, m. p. 123°, were obtained. This material was pure, the m. p. not being raised by crystallisation from ethanol; $[\alpha]_D^{16°}$ (methanol–water, 2 : 3) showed downward mutarotation, from + 7·8° to + 3·9° (const. after 24 hours) (*c*, 1·29). In chloroform solution (*c*, 5·9) similar behaviour was observed, $[\alpha]_D$ falling from + 8·7° to a constant value (24 hours) of + 5·7°.

(*d*) *d*-Fructose (5 g.). The crude product was treated with cold 0·1N-sulphuric acid for 6 hours. The yield of pure material (from ligroin, b. p. 60—80°) was 5·40 g. (75·8%), m. p. 95°, $[\alpha]_D^{16°}$ (chloroform) — 24·6° (*c*, 3·9).

(*e*) *l*-Fucose. 535 Mg. yielded 670 mg. (84%) of syrup which crystallised (needles), m. p. 35—37°.

Distillation in a high vacuum failed to raise the m. p. Recrystallisation was readily effected from 50% aqueous methanol, yielding needles, m. p. 35—36°, $[\alpha]_D^{16°}$ (chloroform) + 53·6° (*c*, 2·35).

(*f*) *l*-Arabinose (5 g.). Crude yield, crystalline, 6·59 g. (86%). Recrystallised from water, the substance, 4·80 g. (66·5%) had m. p. 41—42° and $[\alpha]_D^{16°}$ (water) + 5·4° (*c*, 2·88), (chloroform) − 13·2° (*c*, 4·2).

(*g*) *d*-Xylose (2 g.). Crude yield (syrup) 1·82 g. (59·5%), $[\alpha]_D^{16°}$ (water) + 13·0° (*c*, 1·32), (chloroform) + 5·0° (*c*, 2·68).

(*h*) *d*-Ribose. 270 Mg. yielded 129 mg. of a syrupy " monoacetone " condensation product.

Although a reasonable yield is in each instance obtainable by the above procedure, it is emphasised that, the preparation of β-diacetone fructose excepted, methods already described in the literature may for individual examples prove superior.

Recovery of Acetone Sugars after Treatment with Cold 0·1N-*Sulphuric Acid.*—Weighed amounts of the sugars were condensed with acetone (5% sulphuric acid) for 6 hours, and the products, isolated by the procedure described above, subjected to the action of 0·1N-sulphuric acid at room temperature for the times stated. Any material extractable by chloroform was then recovered and weighed. The findings are tabulated below :

Sugar.	Wt. used, mg.	Chloroform-extractable material : Wt., mg. Hrs. in acid : 2.	6.	Yield (%) of sugar taken. 2.	6.	Diacetone cpd. resistant to 0·1N-H_2SO_4, %.
d-Glucose	500	82	0	11·3	0	0
d-Mannose	500	80	0	11·0	0	0
d-Xylose	500	49	0	6·4	0	0
l-Rhamnose	500	55 *	0	8·9 *	0	0
d-Ribose.....	270	—	50 *†	—	14·6 *	—
d-Galactose	390	345	340	68	65	95·6
l-Arabinose	500	663	663	86·4	86·4	100
l-Fucose	535	670	633	84·2	83·3	94·4

* Monoacetone derivatives.

† This material is probably a mixture of 2 : 3-monoacetone ribofuranose with the anhydro-derivative described by Levene and Stiller (*J. Biol. Chem.*, 1933, **102**, 187); sufficient material was not available for accurate investigation.

Monoacetone *d*-ribose is considered by Levene and Stiller (*loc. cit.*) to be substituted in positions 2 and 3 and to have a furanose ring; the behaviour of the crude product described above is intermediate between those compounds which have furanose rings and those resistant substances where the sugar ring is pyranose. It is possible that the acid-resistant portion is the anhydro-fraction of the crude material.

Fission of Sucrose : Separation of d-*Fructose from* d-*Glucose.*—1·00 G. of finely powdered sucrose was shaken for 6 hours with 20 ml. of dry acetone containing 1·25 ml. of sulphuric acid. The crude product, isolated by the customary procedure, was a crystalline mixture of diacetone glucose with the two diacetone fructoses. Treatment of this with 0·1N-sulphuric acid for 6 hours, followed by partition between chloroform and water, yielded 0·66 g. (86·8%) of crystalline material which, after recrystallisation from ligroin (b. p. 60—80°), weighed 0·593 g. (78%) and had m. p. 95° and $[\alpha]_D^{16°}$ (chloroform) − 24·7° (*c*, 5·2).

Separation of β-Diacetone Fructose from a Mixture of Seven Monosaccharides.—A mixture of 200 mg. of each of the following sugars was treated in the manner described for the foregoing experiment : *d*-glucose, *d*-galactose, *d*-mannose, *l*-arabinose, *d*-xylose, *l*-rhamnose, and *d*-fructose. After the acid treatment the crude product became partly crystalline. As it weighed 450 mg. it obviously contained diacetone galactose and diacetone arabinose as well as β-diacetone fructose. The crystals were drained on porous tile, after trituration with ice-cold ligroin (b. p. below 40°); recrystallisation in the usual way yielded 90 mg. of β-diacetone fructose, m. p. 95° alone or mixed with authentic substance.

Separation of Fructose, as the 1 : 2-*Monoacetone Derivative, from a Sugar yielding an Acid-stable Diacetone Derivative.*—If the mixture of sugars is condensed with acetone containing 0·3% of sulphuric acid as catalyst, as noted above, the fructose yields the acid-unstable α-diacetone derivative. (Galactose and arabinose yield 11% and 90% of their respective diacetone derivatives.) A mixture of 1·008 g. of α-diacetone fructose with 1·046 g. of diacetone galactose was kept in 0·1N-sulphuric acid solution for 4 hours at 16°. The unchanged diacetone galactose was extracted with chloroform, as in preceding experiments. The aqueous phase was made alkaline (phenolphthalein) with potassium hydrogen carbonate and heated at 100° for 30 minutes to destroy traces of reducing sugar. The solution was then evaporated. and the solid residue extracted three times with 50 ml. portions of boiling, dry ethyl acetate. On evaporation of this extract, 0·76 g. (89%) of nearly pure, crystalline 1 : 2-monoacetone *d*-fructose was obtained; m. p. 119°, $[\alpha]_D^{17°}$ (water) − 158·8°. After recrystallisation from dry ethyl acetate, the m. p. rose to 121—122° and $[\alpha]_D^{17°}$ (water) was − 159·4° (*c*, 3·4). From the chloroform phase of the partition 0·981 g. of diacetone *d*-galactose was recovered after evaporation of the solvent.

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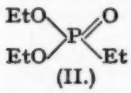
278. *The Reaction between Trialkyl Phosphites and Alkyl Halides.*

By A. H. Ford-Moore and J. Howarth Williams.

The rearrangement of trialkyl phosphites (Arbusov) has been extended so as to afford a simple method for preparing the dialkyl esters of alkyl- and halo-alkyl-phosphonic acids. When the halogen (bromine) atom in diethyl halogeno-alkylphosphonates is in the β-position to the phosphorus, hydrogen bromide is readily lost, giving dialkyl alkylenephosphonates.

The Arbusov rearrangement in its simplest form (*Chem. Zentr.*, 1906, II, 1640) consists of the isomerisation of a trialkyl phosphite to a dialkyl alkylphosphonate (in 95% yield) by warming it with the corresponding alkyl iodide. Arbusov and Kushkova (*J. Gen. Chem. Russia*, 1936, **6**, 283) extended the reaction to methylene iodide and found that when this compound was heated with triethyl phosphite (I), diethyl iodomethylphosphonate could be isolated from the reaction mixture.

Later, Kosolapoff (*J. Amer. Chem. Soc.*, 1944, **66**, 1511) reinvestigated the reaction between (I) and butyl bromide, hexyl bromide, ethylene bromide, and trimethylene bromide. He found that when the first three bromides were heated with (I), ethyl bromide was eliminated and some diethyl ethylphosphonate (II) formed. He was unable to isolate any other product of the reaction. With trimethylene bromide, he obtained some tetraethyl trimethylenediphosphonate and diethyl 3-bromopropylphosphonate, the latter as the free acid after hydrolysis.

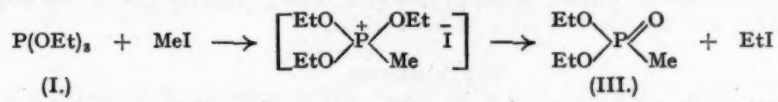

(II.)

In our hands, the Arbusov rearrangement was found to be of much wider application and can be used for preparing several series of compounds. In all cases except one (in which tri*iso*propyl phosphite was used), the reaction was carried out with (I).

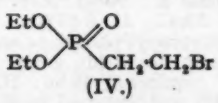
When (I) is warmed with an equimolar quantity of methyl iodide for a short time, a vigorous reaction sets in, and, on fractionation of the product, almost quantitative yields of ethyl iodide and diethyl methylphosphonate (III) are obtained. The reaction between methyl iodide and tri*iso*propyl phosphite proceeds even more easily, the products being *iso*propyl iodide and di*iso*propyl methylphosphonate.

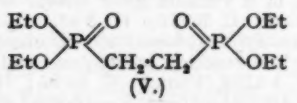
The interaction of (I) and ethylene bromide was next examined. If the reaction is carried out under reflux, the mixture on fractionation gives ethyl bromide, a considerable amount of (II), and a high boiling residue.

The reaction between (I) and methyl iodide gives strong support to the suggestion that the rearrangement takes place through the formation of an unstable phosphonium halide. In this particular case, the larger radical is eliminated as halide:


(I.) (III.)

It seemed probable, therefore, that, in the reaction between (I) and ethylene bromide, if the ethyl bromide were allowed to escape, the amount of high-boiling residue formed would increase at the expense of the (II). This was found to be so. When the reaction was carried out under a column so that the ethyl bromide distilled out as fast as it was formed, the residue of high-boiling material was considerably greater. This, on further distillation at 1—2 mm., was found to be a mixture of diethyl 2-bromoethylphosphonate (IV) and tetraethyl ethylene-


(IV.)

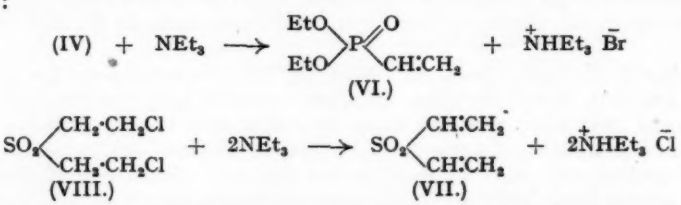

(V.)

1 : 2-diphosphonate (V). Contrary to the observation of Kosolapoff (*loc. cit.*), they both appear to distil at this pressure without decomposition.

This reaction can be extended to primary alkyl bromides. With *n*-hexyl bromide or higher homologues, the reaction proceeds very smoothly giving ethyl bromide and a small amount of (II), most of the product consisting of the diethyl alkylphosphonate, isolated by distillation in a vacuum. The reaction of (I) with *n*-amyl bromide goes less easily; with *n*-butyl bromide and *iso*amyl bromide, it takes place very sluggishly; ethyl bromide is slowly evolved, a considerable amount of (II) is formed, and the yield of alkylphosphonate is poor. No reaction between secondary bromides, such as *cyclo*hexyl bromide and 2-bromo-octane, and (I) takes place.

When methylene bromide is used, the reaction goes slowly and a poor yield of tetraethyl methylenediphosphonate results, the bromomethylphosphonic ester being almost entirely absent. No difficulty is experienced in obtaining the methylenediphosphonate when methylene iodide is used in place of the bromide, the iodomethylphosphonic ester being formed simultaneously (cf. Arbusov and Kushkova, *loc. cit.*). With trimethylene bromide, we had no difficulty in obtaining tetraethyl trimethylenediphosphonate, but we were unable to prepare the bromopropylphosphonate either pure or in any quantity.

(IV) undergoes an interesting reaction on treatment with triethylamine in dry benzene. Triethylamine hydrobromide is formed, and diethyl vinylphosphonate (VI) can be isolated from the residue by distillation under reduced pressure. This reaction recalls the preparation of divinyl sulphone (VII) from 2 : 2′-dichlorodiethyl sulphone (VIII) (Alexander and McCombie, *J.*, 1931, 1913) :



Unlike (VII), which reacts with thiophenol with evolution of heat [to give 2 : 2′-bis(phenylthioethyl) sulphone], no reaction takes place between thiophenol and (VI).

Since secondary bromides do not enter into this reaction, we hoped to prepare diethyl 2-bromopropylphosphonate (IX) by the interaction of propylene bromide and (I); (IX) should lose HBr on treatment with triethylamine to give diethyl propenylphosphonate (X) :

When (I) and propylene bromide are heated, ethyl bromide distils but no trace of (IX) can be isolated, the product consisting of (II) together with a rather poor yield of (X).

The (I) used in these reactions was prepared by the method of McCombie, Saunders, and Stacey (*J.*, 1945, 380) who obtained it by the action of phosphorus trichloride on ethanol in ether in the presence of dimethylaniline. We found that the dimethylaniline could be replaced with advantage by diethylaniline and the ether by light petroleum (b. p. 40—60°). The diethylaniline hydrochloride formed is non-hygroscopic, a 95% recovery of the base is obtained without difficulty, and the yield of (I) is at least 85%.

Experimental.

Triethyl Phosphite (I).—This, prepared in 87—92% yield by the method of McCombie, Saunders, and Stacey (*loc. cit.*) but with light petroleum (b. p. 40—60°) and diethylaniline in place of ether and dimethylaniline, had the following constants : b. p. 52°/14 mm., 57·5°/19 mm. (McCombie, Saunders, and Stacey give b. p. 48°/12·5 mm.), $d_{15°}^{19°}$ 0·963, $n_D^{17·5°}$ 1·4140.

Tri*iso*propyl phosphite was prepared similarly, but owing to the closeness of its b. p. to that of diethylaniline, an equivalent amount of pyridine, or, better, triethylamine was used in place of the former.

Diethyl Methylphosphonate (III).—(I) (55 g.) and methyl iodide (50 g.) were refluxed gently for 2 hours on a steam-bath. On distillation at ordinary pressure, ethyl iodide (50 g.) was recovered. The residue distilled in a vacuum gave *diethyl methylphosphonate* (52·5 g.; 95%), b. p. 64—65°/2 mm., $n_D^{16°}$ 1·4120 (Found : C, 39·18; H, 8·83. $C_5H_{13}O_3P$ requires C, 39·47; H, 8·55%).

Diisopropyl methylphosphonate was obtained similarly from tri*iso*propyl phosphite and methyl iodide in 95% yield. The reaction is vigorous and the conversion complete within a few minutes; b. p. 66°/3 mm., $n_D^{16·5°}$ 1·4120 (Found : C, 45·95; H, 9·53. $C_7H_{17}O_3P$ requires C, 46·66; H, 9·44%).

The Diethyl Alkylphosphonates.—Diethyl ethylphosphonate (II) was prepared in 95% yield by the method of Arbusov (*loc. cit.*) from (I) and ethyl iodide; b. p. 62°/2 mm., $d_{15°}^{21°}$ 1·032, $n_D^{15°}$ 1·4172.

Diethyl n-*dodecylphosphonate.* (I) (62·5 g.) and *n*-dodecyl bromide (94 g.) were heated under a column attached to a condenser set for distillation. At about 160°, ethyl bromide started to distil. After about 1·5 hours, ethyl bromide (31·5 g.) stopped distilling and the mixture was fractionated under reduced pressure to give : (II) (7 g.), b. p. 60—70°/3 mm.; dodecyl bromide (8 g.), b. p. 124°/1 mm.; *diethyl* n-*dodecylphosphonate* (73 g.), b. p. 160°/1 mm., $n_D^{16·5°}$ 1·4419 (Found : C, 62·86; H, 11·60. $C_{16}H_{33}O_3P$ requires C, 62·74; H, 11·51%).

The following esters were obtained similarly. *Diethyl* n-*butylphosphonate*, b. p. 74°/1 mm., $n_D^{17°}$ 1·4244 (Found : C, 47·40; H, 10·21. $C_8H_{19}O_3P$ requires C, 49·49; H, 9·86%). *Diethyl* n-*amylphosphonate*, b. p. 86°/1·5 mm., $n_D^{16·5°}$ 1·4282 (Found : C, 51·12; H, 10·36. $C_9H_{21}O_3P$ requires C, 51·90; H, 10·17%). *Diethyl* n-*hexylphosphonate*, b. p. 103°/2 mm., $n_D^{17°}$ 1·4311 (Found : C, 53·34; H, 10·58 $C_{10}H_{23}O_3P$ requires C, 54·08; H, 10·43%). *Diethyl* n-*heptylphosphonate*, b. p. 113°/1·9 mm., $n_D^{16·5°}$

1·4325 (Found: C, 54·90; H, 10·87. $C_{11}H_{25}O_3P$ requires C, 55·90; H, 10·66%). *Diethyl* n-*octylphosphonate*, b. p. 119°/1·2 mm., $n_D^{16°}$ 1·4360 (Found: C, 57·54; H, 10·88. $C_{13}H_{29}O_3P$ requires C, 57·59; H, 10·88%). *Diethyl* 3-*methyl*-n-*butyl*-1-*phosphonate*, b. p. 75°/0·8 mm., $n_D^{16·5°}$ 1·4266 (Found: C, 51·54; H, 10·26. $C_9H_{21}O_3P$ requires C, 51·90; H, 10·17%).

Diethyl 2-*bromoethylphosphonate* (IV). (I) (83 g. = 0·5 mol.) and ethylene bromide (141 g. = 0·75 mol.) were heated as in the preparation of the dodecylphosphonic ester described above. The reaction was complete in about two hours, 48 g. of ethyl bromide having distilled. The residue on fractionation under reduced pressure gave the following products: recovered ethylene bromide, 77 g.; (II) b. p. 60—70°/3 mm., 15 g.; *diethyl bromoethylphosphonate*, b. p. 101°/0·8 mm., $n_D^{16·5°}$ 1·4600, 48·5 g. (Found: C, 29·71; H, 5·96. $C_6H_{14}O_3BrP$ requires C, 29·40; H, 5·76%); tetraethyl ethylenediphosphonate, (*q.v.*), b. p. 167°/1 mm.

Diethyl iodomethylphosphonate, b. p. 101°/0·7 mm., $n_D^{17°}$ 1·4975 (Found: C, 21·94; H, 4·58. Calc. for $C_5H_{12}O_3IP$: C, 21·60; H, 4·36%) and *tetraethyl methylenediphosphonate*, b. p. 143°/1·5 mm, $n_D^{18·5°}$ 1·4312 (Found: C, 35·68; H, 7·67. $C_9H_{22}O_6P_2$ requires C, 37·51; H, 7·70%) were obtained similarly by substituting methylene iodide for ethylene bromide. Tetraethyl methylenediphosphonate was also obtained by using methylene bromide in place of methylene iodide, but in poor yield; the expected diethyl bromomethylphosphonate was almost entirely absent.

Diethyl vinylphosphonate (VI). (IV) (48·5 g.), triethylamine (22 g. = 30 c.c.), and benzene (70 c.c.) were refluxed for 1 hour. After standing overnight, the triethylamine hydrobromide was filtered off, the benzene distilled from the filtrate, and the residue fractionated under reduced pressure. *Diethyl vinylphosphonate* (26 g.), $n_D^{15°}$ 1·4320, distilled at 63°/2·5 mm. (Found: C, 43·54; H, 8·37. $C_6H_{13}O_3P$ requires C, 43·88; H, 7·98%).

Tetraethyl ethylenediphosphonate (V). (I) (157 g.) and ethylene bromide (100 g. = 47 c.c.) were allowed to react as in the preparation of (IV) and the product was worked up similarly. Ethyl bromide (75 g.) distilled during the reaction, and the residue gave the following fractions: (II), b. p. 55—60°/2 mm., 55 g.; (IV), b. p. 99—115°/1 mm., 18 g.; *tetraethyl ethylenediphosphonate*, b. p. 167°/1 mm. (180°/2·5 mm.), 71 g., $n_D^{16·5}$ 1·4425 (Found: C, 39·26; H, 7·96. $C_{10}H_{24}O_6P_2$ requires C, 39·73; H, 8·00%).

Tetraethyl trimethylenediphosphonate. This was made similarly from (I) and trimethylene bromide; it had b p 175°/0·8 mm., $n_D^{16·5°}$ 1·4508 (Found: C, 40·34; H, 8·18. Calc. for $C_{11}H_{26}O_6P_2$: C, 39·73, H, 8·29%).

When (I) and 1 : 2-dibromopropane were similarly treated, no diethyl 2-bromopropylphosphonate could be isolated. After repeated fractionation under reduced pressure, the product was *diethyl propenylphosphonate* (X), b. p. 78—81°/2 mm., $n_D^{21°}$ 1·4320 (Found: C, 46·60; H, 8·79. $C_7H_{15}O_3P$ requires C, 47·19; H, 8·49%).

The microanalyses were carried out by Mr. W. Brown. The consistently low values found for carbon are probably due to the difficulty in effecting the complete combustion of these substances.

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279. *Lanosterol. Part IV. Hydrocarbons formed by the Action of Dehydrating Agents.*

By Charles Dorée, James F. McGhie, and Frederick Kurzer.

Phosphorus oxychloride and pentachloride have proved effective dehydrating agents in the lanosterol group. Thus, dihydrolanosterol, according to the reagent and conditions employed, yields two isomeric hydrocarbons of the formula $C_{30}H_{50}$, *α-lanostadiene*, and *iso*lanostadiene, respectively. Dihydroagnosterol (γ-lanosterol) and other members of this series are dehydrated with equal facility to the corresponding hydrocarbons. A new alternative method for the preparation of α-lanostene (Ruzicka *et al.*, *Helv. Chim. Acta*, 1944, **27**, 479) is also described, and the relationship between these hydrocarbons is discussed in connection with the position of the unsaturated centres in the molecule.

The experimental facts established in previous researches in regard to lanosterol are the formula, $C_{30}H_{50}O$, and the presence of one secondary hydroxyl group and two double bonds—one reactive and one inert—in a tetracyclic, triterpenoid nucleus, with a side-chain of at least four carbon atoms terminating in an *iso*propylidene group, in which the reactive double bond is incorporated. It was known that the lanosterol fraction obtained from wool-grease contained approximately 10% of the analogous triply unsaturated alcohol agnosterol, $C_{30}H_{46}O$. More recently, Ruzicka *et al.* (*Helv. Chim. Acta*, 1944, **27**, 479; *ibid.*, 1945, **28**, 759) have recognized the presence of both dihydrolanosterol and dihydroagnosterol, and lanosterol has been shown to be identical with the cryptosterol of yeast. The agnosterol compounds can be removed by exhaustive crystallization, leaving a non-separable mixture of lanosterol and its dihydro-derivative, which hitherto has been described as lanosterol. Lanosterol (cryptosterol) has been obtained from this by oxidation, followed by separation and reduction of the ketones. The non-separable mixture, on hydrogenation, yields pure dihydrolanosterol which is suitable for experimental work.

An examination of the hydrocarbons derived from lanosterol and its analogues was undertaken to obtain evidence of the relationship between lanosterol and other tetracyclic triterpenes, and to make available new compounds for structural investigation. The fully saturated parent hydrocarbon lanostane has not yet been obtained. Lanostene, corresponding to lanosterol, and hydrocarbons derived from dihydrolanosterol, dihydroagnosterol (γ-lanosterol), and *iso*dihydrolanosterol have been prepared by Ruzicka *et al.* (*locc. cit.*). The procedure employed in each case was to prepare the ketone, the semicarbazone of which was reduced, according to the Wolff–Kishner method, with sodium and ethanol under pressure. A simple and convenient modification has now been found in the direct reduction of ketone to hydrocarbon, using a modified form of the Clemmensen reaction with amalgamated zinc and hydrochloric acid. Under the conditions of experiment the hydrochloric acid does not cause bond-movement, and good yields of the desired hydrocarbons are readily obtained.

A systematic examination of the action of dehydrating agents on dihydrolanosterol has resulted in a new approach to hydrocarbons containing an additional double bond. In the dehydrations studied, the unsaturated linkage would be introduced by the removal of the hydroxyl group and the hydrogen of an adjacent carbon atom of the ring system. Provided that bond-movement does not take place, therefore, the location of the newly formed double bond is limited with great probability to a single position in the ring containing the hydroxyl group.

Most of the dehydrating agents that have been successfully employed in the case of the sterols and triterpenes were found unsuitable for dehydration in the lanosterol series. Anhydrous copper sulphate in xylene, activated alumina at temperatures up to 250°, *p*-toluenesulphonyl chloride in boiling pyridine, and acetic anhydride–sulphuric acid mixtures failed to yield products of dehydration. On the other hand, the halides and oxyhalides of phosphorus, particularly the oxychloride and pentachloride, proved highly satisfactory, giving hydrocarbons smoothly and in excellent yield.

Phosphorus oxychloride, applied by Heilbron (*J.*, 1935, 1223) in the conversion of lumisterol into lumistatetraene, when acting on dihydrolanosterol under analogous conditions gave a non-homogeneous reaction product from which *α-lanostadiene* was isolated. γ-Lanosterol (dihydroagnosterol) similarly gave a trebly unsaturated hydrocarbon, *γ-lanostatriene*. α-Lanostadiene showed no characteristic absorption in the ultra-violet, but γ-lanostatriene gave absorption maxima almost identical with those of γ-lanosteryl acetate (Bellamy and Dorée, *J.*, 1941, 178), indicating that the system of conjugated double bonds is still present. The newly formed unsaturated linkage is remote from this system, as the characteristic absorption curve is not altered, though the intensities are higher in the case of the hydrocarbon, as shown by the following measurements:

	$\lambda_{max._1}$.	$E^{1\%}_{1\ cm.}$.	$\lambda_{max._2}$.	$E^{1\%}_{1\ cm.}$.	$\lambda_{max._3}$.	$E^{1\%}_{1\ cm.}$.
γ-Lanosteryl acetate	238	300	245	380	250	250
γ-Lanostatriene	237	400	243	440	254	320

Lanostadiene has an increased reactivity due to the additional double bond which, unlike the inert double bond in dihydrolanosterol, shows a reactivity approaching that of an ethylenic linkage. Its probable location in the terminal ring of the triterpene molecule, already suggested by its mode of formation, is supported by the properties of the hydrocarbon. Thus, α-lanostadiene readily adds two atoms of hydrogen in the presence of contact catalysts forming α-lanostene, which is identical with Ruzicka's " dihydrolanostene ", obtained by Wolff–Kishner reduction of dihydrolanostenone semicarbazone. Similarly, α-lanostene rapidly absorbs two atoms of bromine: the addition product is highly labile, however, and decomposes at once forming a halogen-free compound, provisionally designated isomer X. Lanostadiene is readily isomerized by hydrogen chloride yielding β-*lanostadiene*, and it can be dehydrogenated to yield products of still higher unsaturation. The action of either selenium dioxide in anhydrous ethanol or *N*-bromosuccinimide afford excellent yields of *α-lanostatriene*. This triene shows no absorption in the ultra-violet, indicating the absence of a system of conjugated double bonds, and its non-identity with γ-lanostatriene.

Opening of the terminal ring of α-lanostadiene by controlled oxidative fission under various conditions has been attempted, but no crystallisable substances have so far been isolated from the large yields of acidic reaction products obtained.

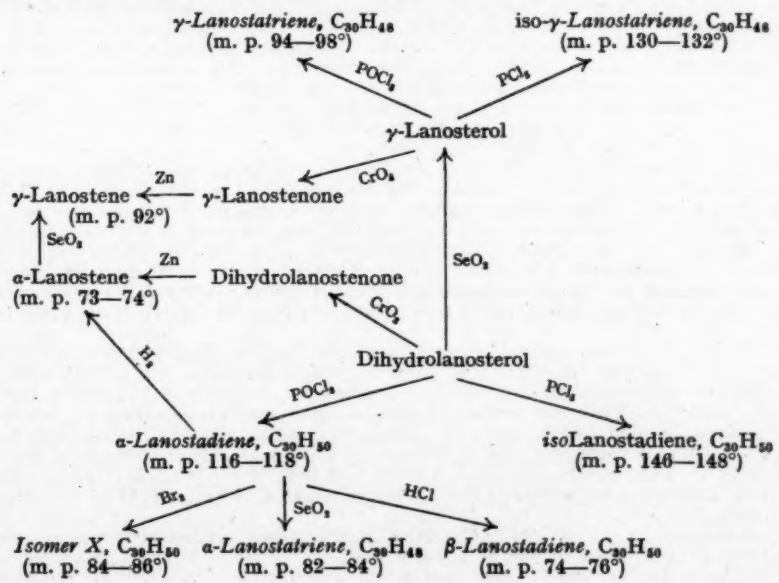
Phosphorus pentachloride has also proved a useful dehydrating reagent. α-Amyranonol, for example, in light petroleum solution is converted into α-amyradienone (Spring and Vickerstaff, *J.*, 1937, 251), while 3(β)-acetoxycholestan-7-" β "-ol can be similarly dehydrated using the reagent in the presence of calcium carbonate in anhydrous media (Wintersteiner and

Moore, *J. Amer. Chem. Soc.*, **1943**, **65**, 1507). Phosphorus pentachloride, acting on dihydrolanosterol in boiling light petroleum solution, gave excellent yields of a doubly unsaturated hydrocarbon, *iso*lanostadiene. Wieland, when dehydrating dihydrocryptosterol by high vacuum distillation with boron trioxide at 350° (Wieland and Joost, *Annalen*, 1941, **546**, 119) obtained a cryptostadiene, $C_{30}H_{50}$. Since the identity of lanosterol and cryptosterol has been established by Ruzicka *et al.* (*Helv. Chim. Acta*, 1945, **28**, 759) and by ourselves, there seems little doubt that *iso*lanostadiene is identical with Wieland's cryptostadiene.

*iso*Lanostadiene and α-lanostadiene, prepared from dihydrolanosterol by the action of phosphorus pentachloride and oxychloride respectively, are isomeric. Unlike α-lanostadiene, *iso*lanostadiene does not undergo hydrogenation, does not readily absorb bromine, and is considerably more resistant to chromic acid oxidation. The double bond in *iso*lanostadiene is therefore far less reactive than that in α-lanostadiene, and its absence from the six-membered terminal ring (presumably owing to bond movement) can be assumed. This view is supported by spectrometric evidence. While α-lanostadiene is transparent over the spectral range in the ultra-violet, *iso*lanostadiene shows a distinct absorption maximum at 235 mμ, suggesting the presence of a system of conjugated double bonds and consequently the close proximity of the centres of unsaturation. If the isomerism of the two products, however, was entirely due to the migration of the reactive double bond of α-lanostadiene under the influence of hydrochloric acid, α-lanostadiene should be readily convertible into the *iso*-compound by treatment with anhydrous hydrogen chloride. As already mentioned, however, α-lanostadiene when treated with either hydrogen chloride or phosphorus pentachloride does not yield *iso*lanostadiene, but an entirely new isomer, β-lanostadiene. The observed facts can therefore not be accounted for by a consideration of geometrical isomerism alone. A retropinacoline rearrangement of the type recently described by Ruzicka *et al.* (*Helv. Chim. Acta*, 1945, **28**, 767, 942, 1628; 1946, **29**, 210), occurring when α-amyranonol, lupeanol, and oleanolic acid lactone are treated with phosphorus pentachloride, may possibly take place in the analogous formation of *iso*lanostadiene. Experiments to obtain further information on the nature of these isomers are in progress.

Phosphorus pentachloride has proved equally satisfactory in the dehydration of related compounds. When applied to γ-lanosterol (dihydroagnosterol), for example, the procedure furnishes good yields of iso-*γ-lanostatriene*.

The relationships of these hydrocarbons are shown in the scheme below:



Experimental.

Melting points are uncorrected. The rotation measurements, for which the authors are indebted to Mr. H. Heath, were made in chloroform solution at 15°.

α-Lanostene ("Dihydrolanostene").—A hot solution of dihydrolanostenone (5 g.; 1 mol.) in glacial acetic acid (150 ml.) was added to amalgamated zinc filings (40 g.; 50 mols.) and the mixture boiled. On

addition of concentrated hydrochloric acid (40 ml.; 30 mols.) vigorous reaction took place, and refluxing was continued for 1½ hours. The clear acetic acid solution was poured into water (600 ml.) and the crude dihydrolanostene, separating as a white flocculent precipitate, isolated by extraction with ether. The extracts were washed with sodium hydroxide solution and with water until neutral, and the colourless oily residue obtained on removal of the solvent further purified by filtration of its petroleum solution through alumina. After 3 recrystallisations from chloroform–methyl alcohol (1 : 5), α-lanostene (2—2·5 g.), m. p. 73—74°, $[\alpha]_D$ + 66·2° (*c*, 0·90), was obtained in lustrous plates (Found: C, 87·58; H, 12·40. Calc. for $C_{30}H_{52}$: C, 87·38; H, 12·62%).

γ-Lanostene.—(*a*) γ-Lanostenone, when treated with amalgamated zinc as described above, gave 40—50% yields of γ-lanostene, forming shining plates, m. p. 89—91°, $[\alpha]_D$ + 77° (*c*, 1·04) (Found: C, 87·99; H, 12·05. Calc. for $C_{30}H_{50}$: C, 87·81; H, 12·19%).

(*b*) A solution of dihydrolanostene (3 g.; 1 mol.) was refluxed with excess of selenium dioxide (3 g.; 4 mols.) in glacial acetic acid (50 ml.) for 2 hours. The separated selenium was removed, and the filtrate deposited crystalline γ-lanostene on cooling and standing. After two recrystallisations from chloroform–ethyl acetate–methyl alcohol (1 : 1 : 4), pure γ-lanostene, m. p. 90—92°, was obtained.

α-Lanostadiene.—To a solution of dihydrolanosterol (10 g.; 1 mol.) in pyridine (100 ml.) excess of phosphorus oxychloride (15 ml.; 7 mols.) was added slowly with shaking. The temperature of the mixture rose sharply to 80°. After being heated on the steam-bath for 1½ hours, the whole was boiled gently for 3 minutes and allowed to cool to room temperature. The dark brown liquid was then slowly treated with water under cooling; the crude reaction product then appeared in suspension. After repeated extraction with ether, the combined extracts were shaken with concentrated hydrochloric acid to remove pyridine, followed by repeated washings with distilled water until nearly neutral. The yellow mobile oil obtained, on removal of the solvent, was taken up in light petroleum (500 ml.) and filtered through a 25 g. alumina column. A clear colourless eluate was obtained. The yellow oil remaining after distillation of the solvent was crystallised from chloroform–acetone–methyl alcohol (30, 30, and 100 ml. respectively) to give good yields (*ca.* 7 g.) of a white microcrystalline mass. The material melted between 95° and 112° (signs of sintering at 85°). After repeated crystallisation from chloroform–methyl alcohol, *α-lanostadiene*, m. p. 114—117°, was obtained in minute white needles (2·5—3 g.). From the mother liquors there resulted a further crop (3—4 g.) of inferior material. The final fractions separated as an uncrystallisable oil (1—2 g.).

α-Lanostadiene forms microcrystalline white needles, m. p. 116—118°, $[\alpha]_D$ + 113° (*c*, 1,040), slightly Beilstein-positive, giving a brown colour with tetranitromethane. It is soluble in chloroform, ethyl acetate, and acetone, sparingly soluble in methyl alcohol and hot glacial acetic acid (Found: C, 87·73; H, 12·26. $C_{30}H_{50}$ requires C, 87·81; H, 12·19%). Lanostadiene is optically transparent in the ultra-violet. It yields no addition product in the Diels–Alder reaction, and the absence of a system of conjugated double bonds may be inferred. It is readily reduced to α-lanostene.

A solution of α-lanostadiene (2·5 g., 1 mol.) in glacial acetic acid (150 ml.) was treated with hydrogen at 100° at ordinary pressure in the presence of finely divided platinum. Absorption of hydrogen took place rapidly, a total of 115 ml. being taken up within 10 minutes (theory, 130 ml.). Shaking was continued for another 30 minutes. After removal of the platinum the filtrate was distilled in a vacuum to small bulk (20 ml.) and the crude reaction product isolated from the residue, previously diluted with water (100 ml.), by extraction with ether. The ethereal extracts were washed with sodium hydroxide solution and with water and the solvent was removed. The residual oil, after filtration of its light petroleum solution through alumina, was crystallised thrice from chloroform–ethyl acetate–methyl alcohol, when α-lanostene was obtained in minute white plates, m. p. 70—74°, $[\alpha]_D$ + 65·7° (*c*, 0·556), showing no depression of the melting point in admixture with α-lanostene obtained by the reduction of dihydrolanostenone (Found: C, 87·62; H, 12·40%).

Isomer X.—α-Lanostadiene (3 g.; 1 mol.), dissolved in anhydrous ether (60 ml.) was treated at 0°, within 5 minutes, with the theoretical amount of bromine dissolved in anhydrous ether (3·7 ml. of 10% v/v solution; 2 g.-atoms). The bromine solution was decolourised instantaneously; after 10 minutes' standing at 0° the ether was removed under reduced pressure, the slightly fuming yellow oil taken up in light petroleum (b. p. 60—80°; 200 ml.) and purified chromatographically. After three crystallisations from ethyl acetate–acetone–methyl alcohol, a halogen-free product, *isomer X*, m. p. 84—86°, $[\alpha]_D$ + 124° (*c*, 0·372), was obtained in colourless lustrous elongated plates; ultra-violet absorption spectrum showed no absorption between 230 and 500 mμ (Found: C, 87·78; H, 12·21. $C_{30}H_{50}$ requires C, 87·81; H, 12·19%).

α-Lanostatriene.—(*a*) α-Lanostadiene (4 g.; 1 mol.) dissolved in ethanol (350 ml.) was treated with excess of selenium dioxide (3 g.; 3 mols.) and refluxed gently for 8 hours. The solvent was removed in a vacuum, the dark brown residue taken up in ether, and freed from traces of selenium by extraction with sodium cyanide solution. The crude reaction product in light petroleum solution was filtered through a comparatively large alumina column (30 g.). The intense yellow colour of the eluate, however, was retained after two such purifications. On crystallisation of the residue from chloroform–acetone–methyl alcohol, *α-lanostatriene*, m. p. 82—84°, $[\alpha]_D$ + 138° (*c*, 0·796), was obtained in pale yellow needles; no characteristic absorption between 230 and 500 mμ (Found: C, 88·12; H, 11·83. $C_{30}H_{48}$ requires C, 88·23; H, 11·76%).

(*b*) α-Lanostadiene (2·5 g.; 1 mol.), dissolved in anhydrous carbon tetrachloride (60 ml.), was refluxed with excess of *N*-bromosuccinimide (1·5 g.; 1·6 mols.) for 1½ hours. Hydrogen bromide was given off throughout the reaction. After cooling, the succinimide was removed, the filtrate washed until neutral and concentrated. The oily residue was purified through an alumina column, and, after three recrystallisations from chloroform–acetone–methyl alcohol, gave α-lanostatriene in lustrous needles, m. p. 82—84°, $[\alpha]_D$ + 136° (*c*, 0·362), identical with the product obtained by selenium dioxide dehydrogenation.

β-Lanostadiene.—α-Lanostadiene (2·5 g.), dissolved in anhydrous chloroform (50 ml.), was boiled under reflux, and hydrogen chloride passed through the solution for 3 hours. The clear green liquid obtained was washed until neutral and concentrated under reduced pressure. The residual oil, after

purification through alumina of its light petroleum solution, was crystallised thrice from chloroform–acetone–methyl alcohol, when *β-lanostadiene* was obtained in white needles, m. p. 74—76°, $[\alpha]_D$ + 128° (*c*, 0·806); no characteristic absorption between 230 and 500 mμ (Found: C, 87·75; H, 12·28. $C_{30}H_{50}$ requires C, 87·81; H, 12·19%).

γ-Lanostatriene.—γ-Lanosterol (3 g.; 1 mol.), dissolved in pyridine (30 ml.) was treated with excess of phosphorus oxychloride (6 ml.; 10 mols.) at 100° for 1½ hours. On isolation of the product as described under α-lanostadiene, colourless lustrous plates of *γ-lanostatriene* were obtained in 60% yield, m. p. 94—98°, $[\alpha]_D$ + 133° (*c*, 0·568) (Found: C, 88·06; H, 11·93. $C_{30}H_{48}$ requires C, 88·23; H, 11·76%). Ultra-violet absorption spectrum: Maxima at 237, 243, 254 mμ; ($E^{1\%}_{1\,cm.}$ = 400, 440, and 320 respectively), giving an absorption curve practically identical with that of γ-lanosteryl acetate (*J.*, 1941, 178).

iso*Lanostadiene.*—Dihydrolanosterol (10 g.; 1 mol.) dissolved in light petroleum (150 ml., b. p. 60—80°), was treated with excess of phosphorus pentachloride (10 g.; 2 mols.). Reaction took place with warming, and, after 2 hours at room temperature, dehydration was completed by refluxing for 1 hour on the steam-bath. The phosphorus pentachloride dissolved rapidly, hydrogen chloride being evolved throughout the reaction. The clear liquid was allowed to cool, diluted with an equal volume of ether (200 ml.), and freed from excess of acid by several washings with water. After drying, the solution of the crude reaction product in light petroleum was filtered through alumina and the residue obtained after evaporation of the solvent crystallised three times from chloroform–methyl alcohol. Yield, 75—85%.

*iso*Lanostadiene forms lustrous needles, m. p. 146—148°, $[\alpha]_D$ + 66·4° (*c*, 0·950), slightly Beilstein-positive, and giving a brown colouration with tetranitromethane (Wieland and Joost, *loc. cit.*, give m. p. 141—142° for cryptostadiene). It is soluble in chloroform, acetone, and ethyl acetate, sparingly soluble in methyl alcohol; like α-lanostadiene, and in contrast to the other members of the lanosterol group, it is sparingly soluble in hot glacial acetic acid (Found: C, 87·80; H, 12·18. Calc. for $C_{30}H_{50}$: C, 87·81; H, 12·19%). Ultra-violet absorption spectrum: maximum at 235 mμ.

iso-*γ-Lanostatriene.*—γ-Lanosterol (6 g.; 1 mol.), dissolved in light petroleum (120 ml.; b. p. 60—80°) and treated with excess of phosphorus pentachloride (6 g.; 2 mols.) as described for *iso*lanostadiene, gave good yields (60%) of iso-*γ-lanostatriene*, m. p. 130—132°, $[\alpha]_D$ + 11° (*c*, 1·100), in colourless lustrous plates (Found: C, 88·14; H, 12·01. $C_{30}H_{48}$ requires C, 88·23; H, 11·76). Ultra-violet absorption spectrum: maxima at 235, 242, and 251 mμ ($E^{1\%}_{1\,cm.}$ = 420, 450, and 340 respectively). Apart from higher intensities, the absorption curve was identical with that of γ-lanosteryl acetate.

CHELSEA POLYTECHNIC, LONDON, S.W. 3. [*Received, January 14th*, 1947.]

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280. *Aliphatic Nitro-compounds. Part I. Preparation of Nitro-olefins by Dehydration of 2-Nitro-alcohols.**

By G. D. BUCKLEY and C. W. SCAIFE.

Nitroethylene and 1- and 2-nitroprop-1-ene are obtained in good yield by heating the appropriate nitro-alcohol with phthalic anhydride. The nitro-olefins are readily polymerised by alkali and decompose on heating; 2-nitroprop-1-ene decomposes rapidly even at room temperature.

ALTHOUGH β-nitrostyrene and its analogues have long been easily accessible, it is only within the last few years that satisfactory preparative methods for the purely aliphatic nitro-olefins have been described.

Four general methods are available all of which involve 2-nitroalkyl esters as intermediates: (*a*) reaction of olefins with nitrogen peroxide followed by treatment of the product with alkali (Levy and Scaife, *J.*, 1946, 1100), (*b*) treatment of 2-nitroalkyl esters with mild alkali (Schmidt and Rutz, *Ber.*, 1928, **61**, 2142; Nightingale and Janes, *J. Amer. Chem. Soc.*, 1944, **66**, 352), (*c*) pyrolysis of 2-nitroalkyl benzoates (Blomquist, Tapp, and Johnson, *J. Amer. Chem. Soc.*, 1945, **67**, 1519), and (*d*) distillation of the 2-nitroalkyl acetates with a trace of sodium or potassium acetate (U.S.P. 2,257,980). The first two methods are not applicable to the preparation of nitroethylene and the nitropropenes owing to the ready polymerisation of the product.

The direct dehydration of nitro-alcohols to nitro-olefins, though well known in the case of 2-nitro-1-aryl alcohols, has hitherto been effected with only one aliphatic nitro-alcohol, 2-nitroethyl alcohol, which by treatment with potassium hydrogen sulphate gave a 50% yield of nitroethylene; this, however, cannot be used for more than a few grams of material at a time (Wieland and Sakellarios, *Ber.*, 1919, **52**, 898).

Attempts to dehydrate 2-nitro-*n*-propyl alcohol with phosphoric oxide, potassium hydrogen sulphate, sulphuric acid, or zinc chloride failed to give any 2-nitropropene.

When the alcohol was heated with phthalic anhydride at 170° under a short column (to hold back unchanged material) at reduced pressure, a mixture of water and 2-nitroprop-1-ene

* Patent application pending.

(50—60% yield) distilled. 2-Nitroethyl and 2-nitro*iso*propyl alcohol under similar conditions gave nitroethylene and 1-nitroprop-1-ene respectively in 65—70% yield. The highest yields were obtained by using equimolecular parts of phthalic anhydride and nitro-alcohol, but, as the water formed distilled from the reactants, it was possible to reduce the anhydride to as little as 10 mol. %. Substituted phthalic anhydrides were equally effective.

Nitroethylene was obtained as a pale yellow lachrymatory oil which was moderately stable to heat and light but darkened slowly on keeping. It polymerised readily on treatment with water (cf. Wieland and Sakellarios, *loc. cit.*) and violently in presence of a trace of alkali. 2-Nitroprop-1-ene (Blomquist *et al.*, *loc. cit.*) was a pale yellow lachrymatory oil which rapidly turned green and decomposed to a black tar on being kept for a few days even in the dark; no means of arresting this decomposition was discovered. It decomposed vigorously on warming to 100° to give a complex mixture of products, and polymerised readily on treatment with alkalis. 1-Nitroprop-1-ene (Levy and Scaife, *loc. cit.*) resembled the two nitro-olefins described above, but was much more stable. It was apparently unchanged after one year's storage, and was unaffected by water, but polymerised vigorously on treatment with alkali, and decomposed on attempted distillation under atmospheric pressure.

Experimental.

Nitroethylene.—2-Nitroethyl alcohol (100 g.) (Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) and phthalic anhydride (180 g.) were mixed in a distillation apparatus fitted with a short fractionating column and heated by means of an oil-bath The apparatus was evacuated to 80 mm. and the bath temperature maintained at 140—150° until the mixture was homogeneous. The bath temperature was then raised to 175° and held at 175—180° until distillation ceased. The distillate was dried ($CaCl_2$) and re-distilled, giving nitroethylene (55 g.; 66·5% theory) as a pale yellow oil, b. p. 38—39°/80 mm.

1-*Nitroprop*-1-*ene.*—2-Nitro*iso*propyl alcohol (105 g.) (Levy and Scaife, *loc. cit.*) was brought into reaction with phthalic anhydride (150 g.) at 180°/50 mm. as described above for 2-nitroethyl alcohol. 1-Nitroprop-1-ene was obtained as a pale yellow oil (58·5 g.; 67% theory), b. p. 54°/28 mm.

2-*Nitroprop*-1-*ene.*—2-Nitro-*n*-propyl alcohol (105 g.) (Vanderbilt and Hass, *Ind. Eng. Chem.*, 1940, **32**, 34) was brought into reaction with phthalic anhydride (150 g.) at 175—180°/80 mm. as described above to give 2-nitroprop-1-ene as a pale yellow oil (48·5 g.; 55·5% theory), b. p. 58°/90 mm.

The authors wish to thank Dr. A. Lowe and Mr. R. H. Stanley for suggestions and assistance in carrying out this work, and Dr. N. Levy and Dr. H. A. Piggott for their interest and advice.

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281. *Aliphatic Nitro-compounds. Part II. Conjugated Nitro-dienes.*

By G. D. Buckley and (Mrs.) J. L. Charlish.

Three conjugated nitro-dienes, *viz.* : 3-*nitropenta*-1 : 3-*diene*, 2-*nitro*-3-*methylbuta*-1 : 3-*diene* and 1-(1-*nitrovinyl*)cyclo*hexene* have been synthesised. These compounds are very unstable, and preliminary experiments on their addition reactions have yielded no identifiable products. 1-(1-Nitrovinyl)*cyclo*hexene readily forms a crystalline *dimeride* of unknown constitution.

In view of the high reactivity of the α-nitro-olefins, it seemed likely that conjugated nitro-dienes, if they could be prepared, would form a useful starting point for novel synthesis. No attempt to prepare compounds of this type appears to be recorded in the literature, and it was therefore decided to apply to the problem the methods which are successful in the synthesis of the nitro-olefins.

During the preparation of 2-nitro*iso*propyl acetate by acetylation of crude 2-nitro*iso*propyl alcohol formed by interaction of nitromethane and acetaldehyde (Henry, *Bull. Soc. chim.*, 1895, **13**, 999), a large quantity of a high-boiling by-product was accumulated which on fractionation gave a mixture of diastereoisomerides of 3-*nitro*-2 : 4-*diacetoxypentane* (I), one of which was isolated in a pure crystalline state. On being heated with a small amount of sodium acetate, this material readily underwent fission to 3-*nitropenta*-1 : 3-*diene* (II) and acetic acid.

$$\underset{\text{(I.)}}{NO_2\cdot CH(CHMe\cdot O\cdot CO\cdot CH_3)_2} \longrightarrow \underset{\text{(II.)}}{CH_3\cdot CH{:}C(NO_2)\cdot CH{:}CH_2} + CH_3\cdot CO_2H$$

Like the simple nitro-olefins, the nitro-diene was a powerful lachrymator and very unstable. It decomposed to a black tar under the influence of light or heat, even in the presence of quinol, but was apparently unchanged after several weeks in the dark. It did not polymerise on treatment with alkalis but was readily polymerised by peroxides to a dark brown low-melting

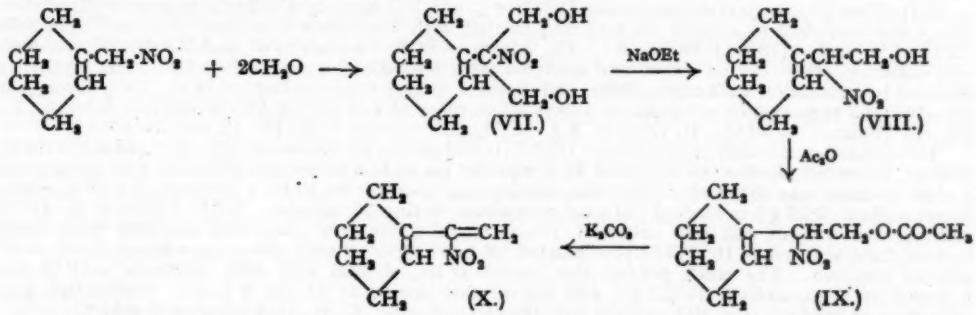
solid. It failed to react with aqueous sodium hydrogen sulphite and gave only tars on being warmed with maleic anhydride or *cyclo*pentadiene. With bromine in carbon tetrachloride a dark oil was obtained which could not be purified; with piperidine an adduct was formed, but this was not further investigated.

2-*Nitro*-3-*methylbuta*-1 : 3-*diene* was prepared from 1-nitro-2-methylprop-2-ene by the following series of reactions.

$$CH_2{:}CMe{\cdot}CH_2{\cdot}NO_2 + 2CH_2O \longrightarrow \underset{\text{(III.)}}{CH_2{:}CMe{\cdot}C(NO_2)(CH_2{\cdot}OH)_2} \xrightarrow{NaOEt} \underset{\text{(IV.)}}{CH_2{:}CMe{\cdot}CH(NO_2){\cdot}CH_2{\cdot}OH} \xrightarrow{Ac_2O} \underset{\text{(V.)}}{CH_2{:}CMe{\cdot}CH(NO_2){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3} \xrightarrow{NaOAc} \underset{\text{(VI.)}}{CH_2{:}CMe{\cdot}C(NO_2){:}CH_2}$$

The *diol* (III) on treatment with sodium ethoxide afforded the *alcohol* (IV) (cf. Schmidt and Wilkendorf, *Ber.*, 1919, **52**, 389). Both the diol and the alcohol were difficult to purify, but for the preparation of (VI) this was immaterial, provided that the more stable *acetate* (V) was fractionated. The diene (VI) closely resembled the isomeric 3-nitropenta-1 : 3-diene in its properties but was even less stable, decomposing to a black tar on standing for a few days.

Application of these syntheses to 1-nitromethyl*cyclo*hexene gave 1-(1-*nitro*-2-*acetoxyethyl*)-cyclo*hexene* (IX), but attempted distillation of this with sodium acetate resulted in violent decomposition. A similar result was obtained on attempting to dehydrate the *alcohol* (VIII) by distillation with 3-nitrophthalic anhydride.



By treating the nitro-ester (IX) in ether with potassium carbonate in presence of quinol a lachrymatory oil, presumably (X), was obtained, but this could not be purified. On standing it gave a solid which (from analysis and molecular weight) appeared to be a *dimeride* of (X). This product was also obtained directly if the potassium carbonate treatment was carried out in the absence of quinol. The yield was poor, but no other pure compounds were isolated. Although other new products were obtained, these could not be purified. Hydrogenation and addition of bromine to the dimer gave no definite products, and no systematic study of its reactions was attempted.

Experimental.

Microanalyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

3-*Nitro*-2 : 4-*diacetoxypentane* (I).—The high-boiling residue (700 g.) from a series of preparations of 2-nitro*iso*propyl acetate (prepared by acetylation of the crude nitro-alcohol from acetaldehyde and nitromethane; cf. Schmidt and Rutz, *Ber.*, 1928, **61**, 2142) was fractionated to give a viscous yellow oil (490 g.), b. p. 140—150°/20 mm., which partly crystallised on standing. The solid *compound* was collected and recrystallised from light petroleum (b. p. 100—120°), forming colourless needles (40 g.), m. p. 85—86° (Found : C, 46·6; H, 5·95; N, 6·2. $C_9H_{15}O_6N$ requires C, 46·35; H, 6·4; N, 6·0%).

The liquid fraction was apparently essentially a mixture of the two diastereoisomerides (Found : C, 46·05; H, 6·25; N, 6·6%).

3-*Nitropenta*-1 : 3-*diene* (II).—Crude 3-nitro-2 : 4-diacetoxypentane (145 g.) was stirred with anhydrous sodium acetate (1 g.) at 95—100° for 1 hour and distilled under 12 mm. The distillate was washed thrice with saturated brine, dried, and fractionated to give 3-*nitropenta*-1 : 3-*diene* (38 g.; 54% theory) as a pale yellow lachrymatory oil, b. p. 63—65°/13 mm. (Found : C, 53·25; H, 6·3; N, 12·35. $C_5H_7O_2N$ requires C, 53·1; H, 6·2; N, 12·4%). A considerable tarry residue remained after the distillation.

2-*Nitro*-1-*hydroxy*-3-*methyl*-2-*hydroxymethylbut*-3-*ene* (III).—A mixture of 1-nitro-2-methylprop-2-ene (2 g.; Levy and Scaife, in the press), ethyl acetate (6 c.c.), paraformaldehyde (1·3 g.), and 33% aqueous potassium hydroxide (1 drop) was refluxed until all the paraformaldehyde had dissolved. The solution was kept at 0° for several days, and the crystalline precipitate collected and purified by recrystallisation from ethyl acetate, giving colourless rectangular prisms of the *compound*, m. p. 103—104° (Found : C, 44·75; H, 6·55; N, 8·5. $C_6H_{11}O_4N$ requires C, 44·7; H, 6·8; N, 8·7%).

2-Nitro-1-hydroxy-3-methylbut-3-ene (IV).—A mixture of 1-nitro-2-methylprop-2-ene (20 g.), *iso*propyl alcohol (60 c.c.), paraformaldehyde (13·2 g.), and 33% aqueous potassium hydroxide (6 drops) was refluxed for 3 hours. After cooling, a solution of sodium ethoxide [from sodium (5 g.) in alcohol (50 c.c.)] was added slowly with stirring below 10°. After 1 hours' stirring at 0—10°, the precipitate was collected, dissolved in a little water, acidified with dilute hydrochloric acid below 15°, saturated with salt, and extracted with ether. The extract was dried and fractionated to give the *compound* as a colourless oil (5·2 g.), b. p. 113—115°/15 mm. (Found : C, 45·55; H, 7·05; N, 10·1. $C_5H_9O_3N$ requires C, 45·8; H, 6·85; N, 10·7%); distillation was stopped at this point owing to incipient decomposition of the residue.

2-Nitro-1-acetoxy-3-methylbut-3-ene (V).—1-Nitro-2-methylprop-2-ene (24 g.) was converted into 2-nitro-1-hydroxy-3-methylbut-3-ene as described above. After removal of the ether, the crude product was mixed with acetic anhydride (25·2 g.), heated at 100° for 1 hour, and distilled to give the *compound* as a colourless oil (30·2 g.), b. p. 102—104°/0·5 mm. (Found : C, 49·2; H, 6·3; N, 7·8. $C_7H_{11}O_4N$ requires C, 48·6; H, 6·35; N, 8·1%).

2-Nitro-3-methylbuta-1 : 3-diene (VI).—2-Nitro-1-acetoxy-3-methylbut-3-ene (30 g.) and anhydrous sodium acetate (0·1 g.) were heated under 12 mm. (oil-bath temperature 110—120°). A colourless liquid distilled, but after a short time the residue began to decompose and distillation was stopped. The distillate was washed thrice with saturated brine, dried, and distilled to give *2-nitro-3-methylbuta-1 : 3-diene* as a pale yellow lachrymatory oil (4·7 g.), b. p. 54—57°/14 mm. (Found : N, 12·3. $C_5H_7O_2N$ requires N, 12·4%). This closely resembled 3-nitropenta-1 : 3-diene in all its reactions.

1-(1-*Nitro*-2 : 2′-*dihydroxy*iso*propyl*)cyclo*hexene* (VII).—1-Nitromethyl*cyclo*hexene (7 g.; Fraser and Kon, *J.*, 1934, 604), paraformaldehyde (3·3 g.), ethyl acetate (25 c.c.), and 33% aqueous potassium hydroxide (3 drops) were refluxed until homogeneous (2 hours). The mixture was carefully neutralised with N-hydrochloric acid and the solvent removed under reduced pressure. After being kept in a desiccator for several days, the viscous residue crystallised to a white solid, m. p. 58—61°, which was very soluble in all organic solvents except light petroleum. Attempts to purify this material were unsuccessful.

1-(1-*Nitro*-2-*hydroxyethyl*)cyclo*hexene* (VIII).—Crude 1-(1-nitro-2 : 2′-dihydroxy*iso*propyl)*cyclo*hexene (9 g.) was dissolved in alcohol (25 c.c.) and treated with a solution of sodium ethoxide [from sodium (1·25 g.) in alcohol (15 c.c.)] below 15°. The mixture was then cooled to 0°, and the precipitated sodium salt collected, dissolved in water, and acidified with hydrochloric acid below 15°. The product was isolated by extraction with ether, dried, and distilled to give a pale yellow oil (3 g.; 38% theory), b. p. 98—100°/0·5 mm., which solidified to a crystalline mass of 1-(1-*nitro*-2-*hydroxyethyl*)cyclo*hexene*, m. p. 45—46° (Found : C, 56·05; H, 7·25; N, 8·1. $C_8H_{13}O_3N$ requires C, 56·15; H, 7·6; N, 8·2%).

1-(1-*Nitro*-2-*acetoxyethyl*)cyclo*hexene* (IX).—1-Nitromethyl*cyclo*hexene (21 g.), paraformaldehyde (9·9 g.), *iso*propyl alcohol (45 c.c.), and 33% aqueous potassium hydroxide (0·5 c.c.) were refluxed until a clear solution was obtained. After the solution had been cooled to 0°, a solution of sodium ethoxide [from sodium (3·75 g.) in alcohol (40 c.c.)] was added during 30 minutes. After 1 hour at 0—10° with stirring, the sodium salt was collected, dissolved in water (100 c.c.), and acidified with aqueous hydrochloric acid below 10°. The precipitated oil was extracted with ether, the extract dried, and the solvent removed. The crude *product* was cooled in ice, treated with 98% sulphuric acid (2 drops) followed by acetic anhydride (23 g.), and the mixture stirred at 60° for 2 hours. Distillation gave a colourless oil (22·5 g.), b. p. 102—105°/1 mm. (Found : N, 6·5. $C_{10}H_{15}O_4N$ requires N, 6·55%).

1-(1-*Nitrovinyl*)cyclo*hexene* (X).—1-(1-Nitro-2-acetoxyethyl)*cyclo*hexene (15 g.), potassium carbonate (15 g.), ether (50 c.c.), and quinol (0·1 g.) were refluxed with stirring for 4 hours, cooled, and washed with water. The ethereal solution was then treated with a further 0·1 g. of quinol and dried ($CaCl_2$). The ether was removed under reduced pressure at 30°, leaving a pale yellow lachrymatory oil (9·2 g.) which decomposed on attempted distillation under 0·5 mm. (Found : N, 8·8. $C_8H_{11}O_2N$ requires N, 9·15%). The *nitro-diene* did not react with aqueous sodium hydrogen sulphite and did not polymerise on boiling with dilute sodium carbonate solution; on keeping, it slowly dimerised.

1-(1-*Nitrovinyl*)cyclo*hexene Dimer*.—1-(1-Nitro-2-acetoxyethyl)*cyclo*hexene (48 g.), potassium carbonate (48 g.), and ether (150 c.c.) were refluxed with stirring for 4 hours, cooled, washed with water, and dried ($CaCl_2$). The ethereal solution was allowed to evaporate at 20° and the crystals were collected (9·9 g.) and washed with light petroleum (b. p. 100—120°). Recrystallisation from light petroleum and from acetic acid gave large colourless plates of 1-(1-*nitrovinyl*)cyclo*hexene dimer*, m. p. 136—137° (Found : C, 62·6; H, 7·4; N, 9·3; *M* (cryoscopic in benzene), 290. $C_{16}H_{22}O_4N_2$ requires C, 62·75; H, 7·2; N, 9·15%; *M*, 306).

The authors wish to acknowledge the interest and advice of Dr. H. A. Piggott in this work.

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282. *Aliphatic Nitro-compounds. Part III. Preparation of Alkyl 2-Nitroalkyl Ethers.**

By A. LAMBERT, C. W. SCAIFE, and A. E. WILDER-SMITH.

Alcohols add to α-nitro-olefins giving alkyl 2-nitroalkyl ethers, which on reduction yield amines, and on reaction with formaldehyde afford α-hydroxymethyl derivatives. 1 : 2-Dinitroethane (or 2-nitroethyl nitrate), 1 : 2-dinitropropane, and 1 : 2-dinitro-2-methyl-

* Cf. E.PP. 573,872, 581,134.

propane may be used as convenient substitutes for nitroethylene, 1-nitroprop-1-ene, and 1-nitro-2-methylprop-1-ene respectively.

THE addition of alcohols to some substituted nitro-olefins has been reported previously; thus, β-nitrostyrene (Rosenmund, *Ber.*, 1913, **46**, 1034; Meisenheimer and Heim, *ibid.*, 1905, **38**, 467), β-bromo-β-nitrostyrene (Thiele and Haeckel, *Annalen*, 1902, **325**, 1), 2-nitro-1-(*p*-methoxyphenyl)prop-1-ene (Meisenheimer and Jochelson, *ibid.*, 1907, **355**, 293), 1-bromo-1-nitrobut-1-ene and 1-bromo-1-nitropent-1-ene (Loevenich, Koch, and Pucknat, *Ber.*, 1930, **63**, 636) all add alcohols in the presence of a basic catalyst to give 2-nitroalkyl ethers; benzylidene-ω-nitroacetophenone behaves similarly with boiling alcohol in the absence of a base (Wieland, *Annalen*, 1903, **328**, 189; cf. Friedlander, Mahly, and Lazarus, *ibid.*, 1885, **229**, 210, 234; Flürscheim, *J. pr. Chem.*, 1902, **66**, 16). Since the present work was completed, the preparation of 2-nitroalkyl ethers by reaction of 1-nitrobut-1-ene and some higher nitro-olefins with sodium alkoxides has also been reported (U.S.P. 2,391,815).

The reaction of alcohols with 1 : 2-dinitro-paraffins and 2-nitroalkyl nitrates, obtained from the addition of nitrogen tetroxide to olefins (see Levy *et al.*, *J.*, 1946, 1096, 1100), and with α-nitro-olefins, was undertaken as part of a general investigation of the chemistry of these compounds and as a route to a wide variety of nitro- and amino-ethers. With boiling alcohols, 1 : 2-dinitroethane (or 2-nitroethyl nitrate) and 1 : 2-dinitropropane gave nitro-ethers as follows :

$$\left.\begin{array}{l} NO_2\cdot CH_2\cdot CH_2\cdot NO_2 + ROH \longrightarrow NO_2\cdot CH{:}CH_2 + R\cdot O\cdot NO + H_2O \\ NO_2\cdot CH_2\cdot CH_2\cdot O\cdot NO_2 + ROH \longrightarrow NO_2\cdot CH{:}CH_2 + R\cdot O\cdot NO_2 + H_2O \end{array}\right\} NO_2\cdot CH{:}CH_2 + R\cdot OH \longrightarrow NO_2\cdot CH_2\cdot CH_2\cdot OR$$

The reaction was found to be a general one, but yields diminished with increasing molecular weight of the alcohol and were lower with 2-nitroethyl nitrate than with 1 : 2-dinitroethane. Treatment of 1 : 2-dinitro-2-methylpropane with boiling alcohols gives 1-nitro-2-methylprop-1-ene which adds alcohols only in the presence of a basic catalyst. 2-Nitroprop-1-ene, 2-nitrobut-2-ene, and β-nitro-β-methylstyrene also require a basic catalyst, the highest yields being obtained by the use of an equivalent of the appropriate sodium alkoxide. In the reaction of 2-nitroprop-1-ene with sodium methoxide, in addition to *methyl 2-nitro*-n-*propyl ether*, some methyl 2 : 4-dinitro-2-methylamyl ether was obtained as a by-product, formed by addition of the mononitro-ether to 2-nitropropene (cf. Part VIII in this series) :

$$CH_3\cdot C(NO_2){:}CH_2 + CH_3\cdot OH \longrightarrow CH_3\cdot CH(NO_2)\cdot CH_2\cdot O\cdot CH_3$$

$$CH_3\cdot CH(NO_2)\cdot CH_2\cdot C(CH_3)(NO_2)\cdot CH_2\cdot O\cdot CH_3 \quad (\downarrow\ CH_3\cdot C(NO_2){:}CH_2)$$

β-Nitrostyrene and sodium methoxide have been reported to give a small yield of methyl 2 : 4-dinitro-1 : 3-diphenylbutyl ether by a similar mechanism (Meisenheimer and Heim, *loc. cit.*). Nitroethylene was very reactive; even when stabilised with a small amount of phosphoric acid it added 2-methoxyethyl alcohol at ordinary temperature.

The nitro-ethers were readily hydrogenated to amines, and reaction with formaldehyde in the presence of a base gave α-hydroxymethyl derivatives.

The *2-nitrobut-2-ene* used in this work was obtained from 2-nitro-3-acetoxybutane (Vanderbilt and Hass, *Ind. Eng. Chem.*, 1940, **32**, 34) by heating it with sodium acetate (cf. Gen. Aniline and Film Corp., U.S.P. 2,257,980). Its structure was established by reduction with zinc and acetic acid (cf. Bouveault and Wahl, *Bull. Soc. chim.*, 1903, **29**, 643) to methyl ethyl ketoxime. It is interesting that a product from the decomposition of the silver salt of nitroethane was described by Angeli and Alessandri (*Atti R. Accad. Lincei*, 1910, **19**, 784; *Chem. Zentr.*, 1910, II, 731) as being probably 2-nitrobut-2-ene, but its structure was not proved.

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton and Mr. A. E. Heron. All m. ps. are uncorrected.

Alkyl 2-Nitroalkyl Ethers.

(a) *From 1 : 2-Dinitro-paraffins.—Alkyl 2-nitroethyl ethers.* Methyl and ethyl 2-nitroethyl ethers were prepared by refluxing a 15% solution of 1 : 2-dinitroethane (Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) in the appropriate alcohol for 36 hours. The excess of alcohol was distilled, and the residual crude nitro-ether distilled first in steam at 60 mm. (to avoid the unstable residue formed on distillation) and then in high vacuum. For the higher alkyl 2-nitroethyl ethers, molten 1 : 2-dinitroethane was added to the boiling alcohol, the temperature of the bath being adjusted to distil off the alkyl nitrite as formed. The nitro-ether was then isolated by fractional distillation. The compounds prepared by this method are *methyl* (60% yield), b. p. 38°/1 mm., 67°/12 mm.; $d_4^{20°}$ 1·128; $n^{20°}$ 1·417 (Found : C, 34·7; H, 6·9; N, 13·4. $C_3H_7O_3N$ requires C, 34·3; H, 6·7; N, 13·3%); ethyl (50% yield), b. p. 46°/1 mm.;

72°/12 mm.; $d_4^{16°}$ 1·069 (Henry, *Rec. Trav. chim.*, 1899, **18**, 259, records b. p. 178°/760 mm.; $d_D^{16°}$ 1·148) (Found: C, 40·5; H, 7·5; N, 12·0. Calc. for $C_4H_9O_3N$: C, 40·3; H, 7·6; N, 11·8%); n-*propyl* (45% yield), b. p. 48°/0·5 mm. (Found: N, 10·3. $C_5H_{11}O_3N$ requires N, 10·5%); iso*propyl*, b. p. 43°/0·5 mm. (Found: N, 10·6. $C_5H_{11}O_3N$ requires N, 10·5%); n-*butyl* (27% yield), b. p. 70—72°/2 mm. (Found: N, 9·7. $C_6H_{13}O_3N$ requires N, 9·5%); and n-*amyl* 2-*nitroethyl ether* (39% yield), b. p. 80—82°/1·5 mm. (Found: N, 8·4. $C_7H_{15}O_3N$ requires N, 8·7%).

Methyl nitro-tert.-*butyl ether*. 1 : 2-Dinitro-2-methylpropane (29·6 g.) (Levy and Scaife, in the press) in methyl alcohol (50 c.c.) was added dropwise with stirring during 30 minutes to a solution of sodium methoxide [from sodium (9·2 g.) in methyl alcohol (200 c.c.)]. The product after dilution with water and neutralisation (acetic acid) was extracted with ether and fractionated, giving *methyl nitro*-tert.-*butyl ether* (5·7 g.), b. p. 75°/15 mm. (Found: C, 45·1; H, 8·3; N, 10·8. $C_5H_{11}O_3N$ requires C, 45·1; H, 8·3; N, 10·5%).

Ethyl nitro-tert.-*butyl ether*. 1 : 2-Dinitro-2-methylpropane (29·6 g.), urea (6·0 g.), and alcohol (300 c.c.) were refluxed for 15 hours. Fractionation gave *ethyl nitro*-tert.-*butyl ether* (4·9 g.), b. p. 75°/15 mm. (Found: C, 48·7; H, 8·7; N, 9·3. $C_6H_{13}O_3N$ requires C, 49·0; H, 8·8; N, 9·5%). Some 1-nitro-2-methylprop-1-ene, b. p. 54—58°/11 mm., was also formed, and the alcohol recovered contained acetone, formed by hydrolysis of the dinitro-paraffin.

Methyl 2-*nitroiso*propyl *ether*. 1 : 2-Dinitropropane (30 g.) (Levy and Scaife, *J.*, 1946, 1100) was refluxed with methyl alcohol (70 g.) for 17 hours, and the mixture fractionated, giving *methyl* 2-*nitroiso*propyl *ether* (8 g.), b. p. 36—41°/1 mm., 62°/12 mm. (Found: C, 40·9; H, 7·7; N, 11·5. $C_4H_9O_3N$ requires C, 40·3; H, 7·6; N, 11·8%).

(b) *From Nitro-olefins.*—*2-Nitro-2'-methoxydiethyl ether*. A mixture of nitroethylene (19·7 g.), 2-methoxyethyl alcohol (100 c.c.), and orthophosphoric acid (1 c.c.), after being kept for 1 month at ordinary temperature, was distilled to give 2-*nitro*-2'-*methoxydiethyl ether* (12·5 g.), b. p. 81—84°/0·5 mm. (Found: C, 40·3; H, 7·3; N, 9·6. $C_5H_{11}O_4N$ requires C, 40·3; H, 7·4; N, 9·4%).

Methyl nitro-tert.-*butyl ether*. 1-Nitro-2-methylprop-1-ene (20·2 g.) was added dropwise with stirring during 30 minutes to a solution of an equivalent of sodium methoxide [from sodium (4·6 g.) in methyl alcohol (100 c.c.)] at ordinary temperature. The product, after dilution with water and neutralisation (acetic acid), was extracted with ether and distilled, giving methyl nitro-*tert.*-butyl ether (17·3 g.), b. p. 75°/15 mm.

2-*Nitro*-3-*methoxybutane*. This was prepared as described above from 2-nitrobut-2-ene (101 g.) and sodium methoxide in methyl alcohol. 2-*Nitro*-3-*methoxybutane* was obtained as a colourless liquid, b. p. 61—63°/15 mm. (Found: C, 45·1; H, 8·3. $C_5H_{11}O_3N$ requires C, 45·1; H, 8·3%). The 2-p-*nitrophenylazo*-derivative, from the sodium salt of the nitro-ether and *p*-nitrobenzenediazonium chloride, separated in two forms; *α-form*, fine yellow needles from light petroleum, m. p. 91° (Found: C, 46·6; H, 5·3; N, 19·7. $C_{11}H_{14}O_5N_4$ requires C, 46·8; H, 5·0; N, 19·8%), and *β-form*, red prisms from light petroleum, m. p. 84° (Found: C, 46·8; H, 5·1; N, 19·3%).

Methyl 2-*nitropropyl ether*. This was prepared from 2-nitroprop-1-ene (27 g.; see Part I of this series) and sodium methoxide in methyl alcohol as described above. Distillation gave *methyl* 2-*nitropropyl ether* (15·2 g.) as a colourless oil, b. p. 61—64°/14 mm. (Found: C, 40·6; H, 7·3. $C_4H_9O_3N$ requires C, 40·3; H, 7·6%). Some methyl 2 : 4-dinitro-2-methylamyl ether (4·8 g.), b. p. 92·5°/0·2 mm. (see Part VIII of this series), was also obtained.

Methyl 2-*nitroiso*propyl *ether*. Interaction of 1-nitroprop-1-ene (50 g.; see Part I of this series) with sodium methoxide in methyl alcohol as described above afforded methyl 2-nitro*iso*propyl ether (29 g.), b. p. 62°/12 mm., identical with that obtained from 1 : 2-dinitropropane.

2-*Nitroiso*propyl n-*butyl ether*. 1-Nitroprop-1-ene (25 g.) and a solution of sodium butoxide [from sodium (6·6 g.) in *n*-butyl alcohol (120 c.c.)], brought into reaction at 0—10° and worked up in the usual way, afforded 2-*nitroiso*propyl n-*butyl ether* (28 g.) as a colourless oil, b. p. 98—101°/14 mm. (Found: C, 52·7; H, 9·1; N, 8·6. $C_7H_{15}O_3N$ requires C, 52·2; H, 9·3; N, 8·7%).

Nitro-tert.-*butyl* n-*amyl ether*. 1-Nitro-2-methylprop-1-ene (50 g.) interacted with sodium *n*-amyloxide as described above to afford *nitro*-tert.-*butyl* n-*amyl ether* (26 g.), b. p. 75°/1 mm. (Found: C, 57·7; H, 9·9; N, 7·2. $C_9H_{19}O_3N$ requires C, 57·2; H, 10·0; N, 7·4%).

Methyl 2-*nitro*-1-*phenyl*-n-*propyl ether*. A solution of β-nitro-β-methylstyrene (489 g.; cf. Alles, *J. Amer. Chem. Soc.*, 1932, **54**, 271) in dioxan (150 c.c.) was added to a solution of sodium methoxide [from sodium (10·35 g.) in methyl alcohol (150 c.c.)] at 10° during ½ hour. After being stirred for 2 hours at room temperature, the mixture was diluted with water, acidified (acetic acid), extracted with ether, and distilled. Fractionation gave *methyl* 2-*nitro*-1-*phenyl*-n-*propyl ether* (51·3 g.) as a colourless oil, b. p. 138—141°/16 mm. (Found: C, 61·6; H, 6·5; N, 7·5. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·6; N, 7·2%).

(c) *From* 2-*Nitroethyl Nitrate*.—2-Nitroethyl nitrate (30 g.) was refluxed with alcohol (150 c.c.) for 8 hours. Fractionation gave ethyl 2-nitroethyl ether (15 g.), b. p. 46°/1 mm.

Interaction of Nitroalkyl Ethers with Formaldehyde.

2-*Nitro*-3-*methoxy*-n-*propyl Alcohol*.—A solution of methyl 2-nitroethyl ether (26·25 g.) in alcohol (25 c.c.) was added to a solution of sodium hydroxide (10 g.) in alcohol (150 c.c.). Paraformaldehyde (7·5 g.) was added and the mixture stirred until a homogeneous solution was obtained. The sodium salt which separated was collected, dissolved in water, acidified (acetic acid), and extracted with ether. Distillation afforded 2-*nitro*-3-*methoxy*-n-*propyl alcohol* (13·5 g.), b. p. 99—104°/0·5 mm. (Found: C, 35·2; H, 6·8; N, 10·5. $C_4H_9O_4N$ requires C, 35·6; H, 6·7; N, 10·4%). Reduction of the nitro-alcohol with Adams's platinum catalyst in alcohol at 20°/100 atms. afforded methyl 2-aminoethyl ether, isolated as the *picrate*, m. p. 148—150° (Found: C, 35·9; H, 4·1. $C_3H_9ON,C_6H_3O_7N_3$ requires C, 35·6; H, 4·0%).

2-*Nitro*-2-*methoxymethylpropane*-1 : 3-*diol*.—Methyl 2-nitroethyl ether (9·32 g.) in methyl acetate (20 c.c.) was treated with paraformaldehyde (5·32 g.) and a trace of alcoholic potassium hydroxide.

After neutralisation the product was collected and crystallised from methyl acetate–light petroleum (b. p. 40—60°), giving *2-nitro-2-methoxymethylpropane*-1 : 3-*diol*, m. p. 82·5—83·5° (Found : C, 36·2; H, 6·8; N, 8·4. $C_5H_{11}O_5N$ requires C, 36·4; H, 6·7; N, 8·5%). Reduction of the nitro-diol with Adams's platinum catalyst in alcohol gave 2-amino-2-methoxymethylpropane-1 : 3-diol, isolated as the *picrolonate*, m. p. 219—220° (Found : N, 17·6. $C_5H_{13}O_5N,C_{10}H_8O_5N_4$ requires N, 17·6%).

2-Nitro-2-ethoxymethylpropane-1 : 3-*diol*.—This was prepared from ethyl 2-nitroethyl ether as described above for the lower homologue. The diol was obtained as an undistillable oil, identified as the *di*-p-*nitrobenzoyl* derivative, m. p. 240—241° (Found : C, 50·7; H, 3·7; N, 8·3. $C_{20}H_{19}O_{11}N_3$ requires C, 50·4; H, 4·0; N, 8·8%).

2-Nitro-3-methoxy-2-methyl-n-*butyl Alcohol*.—A mixture of 2-nitro-3-methoxybutane (40 g.), paraformaldehyde (9·1 g.), aqueous sodium hydroxide (1·5 c.c. of 40%), and methyl alcohol (80 c.c.) was stirred overnight at ordinary temperature. After neutralisation with 2N-hydrochloric acid, distillation gave *2-nitro-3-methoxy-2-methyl*-n-*butyl alcohol* (42 g.) as a colourless oil, b. p. 110°/15 mm., 82°/0·5 mm. (Found : C, 43·5; H, 7·7; N, 8·3. $C_6H_{13}O_4N$ requires C, 44·2; H, 7·9; N, 8·6%).

2-Nitro-3-n-*butoxy*-n-*butyl Alcohol*.—2-Nitro*iso*propyl *n*-butyl ether (53 g.) was dissolved in a solution of sodium hydroxide (13·5 g.) in water (100 c.c.) at 10°, and paraformaldehyde (10 g.) was added portionwise with stirring, the temperature being allowed to rise to 32°. After 20 minutes the solution was acidified (2N-hydrochloric acid), concentrated at 40—50° under reduced pressure, filtered, and distilled, giving *2-nitro*-3-n-*butoxy*-n-*butyl alcohol* (53 g.) as a pale yellow oil, b. p. 98°/0·2 mm. (Found : C, 49·9; H, 9·2; N, 7·5. $C_8H_{17}O_4N$ requires C, 50·3; H, 8·9; N, 7·3%). Reduction of the nitro-alcohol (42 g.) in methyl alcohol (700 c.c.) with Raney nickel and hydrogen at 20°/68 atms. (initial pressure) gave *2-amino*-3-n-*butoxy*-n-*butyl alcohol* (27 g.) as a colourless oil, b. p. 90—92°/0·1 mm. (Found : N, 9·1 $C_8H_{19}O_3N$ requires N, 8·7%).

Alkylaminoethyl Ethers.

Methyl 2-Aminoethyl Ether.—Methyl 2-nitroethyl ether (2·0 g.) in alcohol (22 c.c.) was hydrogenated with Adams's platinum catalyst at 20°/100 atms. to give methyl 2-aminoethyl ether, isolated as the *picrate*, m. p. 148—150° (Found : C, 35·9; H, 4·1. $C_3H_9ON,C_6H_3O_7N_3$ requires C, 35·6; H, 4·0%).

Ethyl 2-aminoethyl ether, obtained in 52% yield by similar reduction of ethyl 2-nitroethyl ether, had b. p. 105°; picrolonate, m. p. 208—209° (decomp.) (Found : C, 47·7; H, 5·5; N, 19·6. Calc. for $C_4H_{11}ON,C_{10}H_8O_5N_4$: C, 47·6; H, 5·4; N, 19·8%); picrate, m. p. 121—123° (Found : C, 37·2; H, 4·6; N, 17·8. Calc. for $C_4H_{11}ON,C_6H_3O_7N_3$: C, 37·6; H, 4·4; N, 17·6%). (Meyer, *Ber.*, 1905, **38**, 3130, records m. p. 204° and 122° respectively for these derivatives.)

2-Amino-3-methoxybutane.—2-Nitro-3-methoxybutane (20 g.) was added slowly with stirring to a mixture of iron powder (3·5 g.), ferric chloride (1 g.), concentrated hydrochloric acid (10 c.c.), and water (75 c.c.) at 100°. After being stirred at 100° for 15 hours, the mixture was basified strongly with aqueous sodium hydroxide and distilled in steam. The distillate was neutralised with hydrochloric acid, evaporated to dryness, basified with excess of 50% aqueous potassium hydroxide, and extracted with ether. The dried extract was fractionated, giving *2-amino-3-methoxybutane* (5 g.) as colourless oil, b. p. 114—116° (Found : N, 13·3. $C_5H_{13}ON$ requires N, 13·6%). The *platinichloride* formed orange prisms from methyl alcohol–ether, m. p. 189—190° (decomp.) [Found : Pt, 31·1. $(C_5H_{13}ON)_2,H_2PtCl_6$ requires Pt, 31·6%]; the 2 : 4-*dinitrophenylurea* (cf. McVeigh and Rose, *J.*, 1945, 621) formed yellow prisms from alcohol, m. p. 152—154° (Found : C, 45·9; H, 4·7; N, 17·6. $C_{12}H_{16}O_6N_4$ requires C, 46·1; H, 5·1; N, 17·9%). The same amine was formed in 50% yield by catalytic reduction of the nitro-ether with Raney nickel–methyl alcohol at 50°/120 atms.

2-Nitrobut-2-ene.—2-Nitro-3-acetoxybutane (161 g.; Vanderbilt and Hass, *loc. cit.*) was stirred with anhydrous sodium acetate (0·6 g.) at 100° for 1 hour and then distilled. The acidic distillate was washed successively with brine, aqueous sodium hydrogen carbonate, and brine, and the product fractionated, giving *2-nitrobut-2-ene* (86 g.) as a pale yellow liquid, b. p. 55·5°/15 mm., $n_D^{22^\circ}$ 1·4600 (Found : C, 46·9; H, 6·8; N, 13·8. $C_4H_7O_2N$ requires C, 47·5; H, 6·9; N, 13·8%). Reduction of the nitro-olefin (30 g.) with zinc and acetic acid (cf. Bouveault and Wahl, *loc. cit.*) gave methyl ethyl ketoxime (17 g.), b. p. 140—150°, which with 2 : 4-dinitrophenylhydrazine in hydrochloric acid gave methyl ethyl ketone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic specimen, 115°.

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283. *Aliphatic Nitro-compounds. Part IV. Addition of Thiols to α-Nitro-olefins.**

By R. L. Heath and A. Lambert.

Thiols and hydrogen sulphide react with α-nitro-olefins under basic conditions, giving 2-nitroalkyl sulphides or thiols. The former can be oxidised to 2-nitroalkyl sulphones (also formed from the nitro-olefin and, *e.g.*, sodium *p*-toluenesulphinate) or reduced to 2-aminoalkyl sulphides, which on oxidation give 2-aminoalkyl sulphones. In certain cases the 2-nitro-alcohols or their esters can be used as convenient substitutes for the nitro-olefins.

* Patent application pending.

As a logical extension of the synthesis of alkyl 2-nitroalkyl ethers by interaction of an α-nitro-olefin with an alcohol (see Part III of this series), the addition of thiols and hydrogen sulphide to nitro-olefins was investigated. This addition was found to be of wide application, and was more facile than the corresponding addition of alcohols.

In the presence of sodium methoxide, 2-nitroprop-1-ene and methylthiol gave an 86% yield of *methyl 2-nitropropyl sulphide*; similarly *methyl 2-nitro-1-methylpropyl sulphide* was obtained from 2-nitrobut-2-ene and methylthiol, *2-nitropropyl butyl sulphide* from 2-nitroprop-1-ene and butylthiol, *methyl 2-nitro-1-phenylethyl sulphide* from β-nitrostyrene and methylthiol, and *phenyl 2-nitroisopropyl sulphide* from 1-nitroprop-1-ene and thiophenol.

That thiols add to nitro-olefins with greater facility than do alcohols is well illustrated by the interaction of *n*-butylthiol with 2-nitroprop-1-ene; in the absence of a catalyst, this yielded 20% of 2-nitropropyl *n*-butyl sulphide, whilst only traces of methyl 2-nitropropyl ether are formed by refluxing methyl alcohol and the nitro-olefin; further, interaction of equimolecular proportions of sodium methoxide and 2-nitroprop-1-ene gave, in addition to the expected methyl 2-nitropropyl ether, some methyl 2 : 4-dinitro-2-methylamyl ether, formed by addition of the nitro-ether to unchanged nitro-olefin (cf. Part III of this series), but in the corresponding reaction with sodium thiomethoxide in place of sodium methoxide, this type of side reaction does not occur.

In the presence of piperidine as catalyst, nitro-*tert.*-butyl alcohol behaved as 1-nitro-2-methylprop-1-ene, and with butylthiol afforded *butyl nitro*-tert.-*butyl sulphide*; as in many examples cited in other parts of this series, 2-nitroethyl nitrate could be used as a convenient source of nitroethylene, and reacted with sodium thioalkoxides to give alkyl (or aryl) 2-nitroethyl sulphides. *Methyl*, p-*tolyl*, p-n-*butylphenyl*, and *carboxymethyl 2-nitroethyl sulphides* were prepared by this method, and sodium thiolacetate gave *2-nitroethyl thiolacetate*.

The addition of water to nitro-olefins in the presence of a basic catalyst is known to yield, in certain cases, 2-nitro-alcohols. It has been found that hydrogen sulphide reacts with nitro-olefins more readily than does water, and in the absence of catalysts, 2-nitrothiols are formed many of which react further with the nitro-olefin, giving di-(2-nitroalkyl) sulphides. The yields of thiol and sulphide vary widely from case to case, and are tabulated below.

Nitro-olefin.	Products and yield.
Nitroethylene	2-Nitroethylthiol (18%) and di-(2-nitroethyl) sulphide (48%)
2-Nitroprop-1-ene	2-Nitropropylthiol (7%)
1-Nitro-2-methylprop-1-ene	Nitro-*tert.*-butylthiol (31%) and di(nitro-*tert.*-butyl) sulphide (trace)
2-Nitrobut-2-ene	Di-(2-nitro-1-methylpropyl) sulphide (25%)
β-Nitrostyrene	Di-(2-nitro-1-phenylethyl) sulphide (37%)

The low yield of 2-nitropropylthiol obtained from 2-nitroprop-1-ene was due to the formation of much unstable high-boiling material. In the condensation of 2-nitrobut-2-ene with hydrogen sulphide, some thiol was formed but could not be obtained pure by distillation. The product from β-nitrostyrene was a mixture from which only one stereoisomeride of *di-(2-nitro-1-phenylethyl) sulphide* could be isolated.

In addition to their formation from nitroethylene and hydrogen sulphide, *2-nitroethylthiol* and *di-(2-nitroethyl) sulphide* were also obtained from 2-nitroethyl nitrate with potassium hydrogen sulphide and potassium sulphide respectively, and hydrolysis of 2-nitroethyl thiolacetate (from thiolacetic acid and 2-nitroethyl nitrate) also gave 2-nitroethylthiol in small yield. 1-Nitro-2-methylprop-1-ene and sodium sulphide gave *di(nitro*-tert.-*butyl) sulphide* and nitro-*tert.*-butylthiol.

Oxidation of nitroalkyl sulphides with hydrogen peroxide in acetic acid afforded the nitroalkyl sulphones in good yield. Thus, *p*-tolyl 2-nitroethyl sulphide gave p-*tolyl 2-nitroethyl sulphone*, which is also obtained by reaction of sodium *p*-toluenesulphinate with 2-nitroethyl nitrate or nitroethylene. Catalytic reduction (Raney nickel) of the nitro-sulphones yielded amino-sulphones, and these were also formed by similar reduction of the nitroalkyl sulphides to aminoalkyl sulphides, followed by oxidation with hydrogen peroxide.

Experimental.

Analyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

Methyl 2-Nitro-1-methylpropyl Sulphide.—A solution of sodium methoxide [from sodium (9·6 g.) in methyl alcohol (100 c.c.)] was added slowly with stirring to a solution of methylthiol (24 g.) in methyl alcohol (60 c.c.) at − 5°. 2-Nitrobut-2-ene (42 g.; see Part III of this series) was then added dropwise during 40 minutes with stirring at 0—5°, and, after being stirred for a further hour, the solution was poured into ice–water (400 c.c.), acidified with dilute acetic acid, and extracted with ether. Fractionation

of the dried extract gave *methyl 2-nitro-1-methylpropyl sulphide* (26 g.) as a colourless unpleasant smelling oil, b. p. 91—96°/15 mm. (Found : N, 9·1. $C_5H_{11}O_2NS$ requires N, 9·4%).

Methyl 2-Nitropropyl Sulphide.—2-Nitroprop-1-ene (30 g.; Part I of this series) was brought into reaction with methylthiol (20 g.) as described above. *Methyl 2-nitropropyl sulphide* (40 g.) was obtained as a colourless liquid, b. p. 98—100°/16 mm. (Found : N, 10·2. $C_4H_9O_2NS$ requires N, 10·4%).

Methyl 2-Nitropropyl Sulphone.—Hydrogen peroxide (30%; 45 c.c.) was added quickly with shaking to a boiling solution of methyl 2-nitropropyl sulphide (10 g.) in glacial acetic acid (40 c.c.). The mixture was boiled for 1 hour and evaporated to dryness under reduced pressure at 40—50°. Crystallisation of the residue from benzene gave *methyl 2-nitropropyl sulphone*, m. p. 69—70° (Found : C, 28·8; H, 5·1; N, 7·9. $C_4H_9O_4NS$ requires C, 28·7; H, 5·4; N, 8·4%).

Methyl 2-Aminopropyl Sulphone.—Methyl 2-nitropropyl sulphone (12 g.) in methyl alcohol (600 c.c.) was shaken with Raney nickel and hydrogen (75 atms. initial pressure) at room temperature. Distillation of the product gave methyl 2-aminopropyl sulphone (2 g.) as a viscous pale yellow oil, b. p. 110—120°/0·3 mm.; the residue decomposed. The *benzoyl* derivative formed colourless needles from ethyl acetate, m. p. 154° (Found : N, 5·9; S, 13·9. $C_{11}H_{15}O_3NS$ requires N, 5·8; S, 13·3%).

Phenyl 2-Nitroisopropyl Sulphide.—Thiophenol (10 g.) was added to a solution of sodium (2·1 g.) in methyl alcohol (50 c.c.) at 0°. 1-Nitroprop-1-ene (7·9 g.; Part I of this series) was added dropwise with stirring at 0—5° and the product treated as described above for the preparation of methyl 2-nitro-1-methylpropyl sulphide. *Phenyl 2-nitroisopropyl sulphide* (11·5 g.) was obtained as a colourless liquid, b. p. 110—111°/0·1 mm. (Found : N, 6·9. $C_9H_{11}O_2NS$ requires N, 7·1%).

Methyl 2-Nitro-1-phenylethyl Sulphide.—A solution of sodium methoxide [from sodium (9·2 g.) in methyl alcohol (100 c.c.)] was added slowly with stirring to a solution of methylthiol (21 g.) in methyl alcohol at − 10°. A solution of β-nitrostyrene (29·8 g.) in dioxan (500 c.c.) was then added dropwise with stirring during ½ hour at 10°. After being stirred at room temperature for ½ hour, the mixture was poured into water and extracted with ether. Distillation of the dried ethereal extract gave *methyl 2-nitro-1-phenylethyl sulphide* (19·1 g.) as a yellow oil, b. p. 168—172°/22 mm. (Found : N, 6·7. $C_9H_{11}O_2NS$ requires N, 6·9%).

2-Nitropropyl Butyl Sulphide.—Butylthiol (10·4 g.) was added to a solution of sodium (2·7 g.) in methyl alcohol (50 c.c.) at 0°. 2-Nitroprop-1-ene (10 g.) was then added dropwise with stirring at 0—10° and the product isolated in the usual way. *2-Nitropropyl butyl sulphide* (12 g.) was obtained as a colourless liquid, b. p. 124—128°/13 mm. (Found : N, 7·8. $C_7H_{15}O_2NS$ requires N, 7·9%). The same product was also obtained by interaction of *n*-butylthiol and 2-nitroprop-1-ene in absence of a catalyst. Equimols. of the reactants were warmed in methyl alcohol solution until reaction commenced, heating was discontinued, and the mixture kept for 12 hours, diluted with ether, washed with sodium hydrogen carbonate and with water, and finally distilled, giving 2-nitropropyl butyl sulphide, b. p. 120—130°/16 mm. in 19% yield. Identity was established by oxidation to the sulphone (see below).

2-Nitropropyl Butyl Sulphone.—Prepared from the sulphide by oxidation with hydrogen peroxide in glacial acetic acid, this *sulphone* separated from methyl alcohol in colourless plates, m. p. 36—37° (Found : N, 6·2; S, 14·7. $C_7H_{15}O_4NS$ requires N, 6·7; S, 15·3%).

n-Butyl Nitro-tert.-butyl Sulphide.—A mixture of *n*-butylthiol (7·0 g.), nitro-*tert.*-butyl alcohol (10 g.; see Part XVIII of this series), and piperidine (1 g.) was kept at 20° for 3 days. The mixture was neutralised with 2N-hydrochloric acid, diluted with ether, and washed with water. Distillation of the ethereal solution gave *n-butyl nitro-tert.-butyl sulphide* (8·6 g.) as a colourless liquid, b. p. 124°/11 mm. (Found : C, 50·4; H, 8·6; N, 7·2. $C_8H_{17}O_2NS$ requires C, 50·3; H, 8·9; N, 7·3%).

m-Di(nitro-tert.-butylsulphonyl)benzene.—Dithioresorcinol (14·2 g.) was added with stirring to a solution of sodium methoxide [from sodium (4·6 g.) in methyl alcohol (160 c.c.)] at 0—10°. 1-Nitro-2-methylprop-1-ene (20·2 g.; Levy and Scaife, in the press) was added dropwise at 0—5°, and the mixture stirred at room temperature for a further 2 hours. The product was poured into ice–water, acidified with dilute acetic acid, and extracted with ether. Distillation of the ethereal extract gave a colourless oil (18·1 g.), b. p. 130°/0·5 mm. The sulphur content of this oil (Found : S, 24·7. Calc. for $C_{14}H_{30}O_4N_2S$: S, 18·6%) indicated that it was contaminated with dithioresorcinol. However, on oxidation with hydrogen peroxide in glacial acetic acid pure *m-di(nitro-tert.-butylsulphonyl)benzene* was obtained in 17% yield. It separated from methyl alcohol in colourless needles, m. p. 166—168° (Found : N, 7·1. $C_{14}H_{30}O_8N_2S_2$ requires N, 6·9%).

Methyl 2-Nitroethyl Sulphide.—A solution of methylthiol (9·6 g.) in methyl alcohol (50 c.c.) was added to a solution of sodium methoxide (10·8 g.) in methyl alcohol (30 c.c.) at − 10°. 2-Nitroethyl nitrate (27·2 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) was added dropwise with stirring at − 5°, and, after being stirred for 3½ hours at 0°, the solution was filtered and distilled, giving *methyl 2-nitroethyl sulphide*, b. p. 105°/20 mm., in 80% yield (Found : C, 30·2; H, 5·8; N, 11·1. $C_3H_7O_2NS$ requires C, 29·8; H, 5·8; N, 11·6%).

Methyl 2-Aminoethyl Sulphide.—Methyl 2-nitroethyl sulphide (40 g.) in methyl alcohol (700 c.c.) was hydrogenated over Raney nickel at 50—60° and 100 atms. (initial pressure). Fractionation of the product gave methyl 2-aminoethyl sulphide (20 g.) as a colourless liquid, b. p. 90—91°/114 mm. (Schneider, *Annalen*, 1912, **386**, 337, gives b. p. 146—148°/760 mm.). The picrate had m. p. 119° (Schneider, *loc. cit.*, gives m. p. 119°).

Methyl 2-Nitroethyl Sulphone.—Oxidation of methyl 2-nitroethyl sulphide (12·1 g.) with hydrogen peroxide in boiling glacial acetic acid gave *methyl 2-nitroethyl sulphone* (12·1 g.), colourless needles from alcohol, m. p. 78° (Found : C, 23·3; H, 5·1; N, 9·1. $C_3H_7O_4NS$ requires C, 23·5; H, 4·6; N, 9·1%).

Methyl 2-Aminoethyl Sulphone.—Methyl 2-nitroethyl sulphone (3·06 g.) in methyl alcohol (40 c.c.) was hydrogenated (Raney nickel) at ordinary temperature and pressure. Distillation of the product gave *methyl 2-aminoethyl sulphone* as a colourless liquid, b. p. 160°/0·02 mm., in almost quantitative yield (Found : N, 10·9. $C_3H_9O_2NS$ requires N, 11·4%). The hydrochloride had m. p. 168° (Schneider, *loc. cit.*, gives m. p. 169°), and the benzoyl derivative, m. p. 134° (Schneider, *loc. cit.*, gives m. p. 134°).

p-n-Butylphenyl 2-Nitroethyl Sulphone.—2-Nitroethyl nitrate (16·4 g.) was added dropwise to a stirred solution of sodium thio-*p*-butylphenol (22·6 g.) in methyl alcohol (200 c.c.) at − 10° to − 5°.

After being stirred for 4 hours the mixture was filtered, evaporated to dryness, and extracted with ether. Removal of the ether gave crude *p-n*-butylphenyl 2-nitroethyl sulphide as a colourless syrup which on oxidation with hydrogen peroxide gave p-n-*butylphenyl 2-nitroethyl sulphone* as colourless needles from alcohol, m. p. 91—92° (Found: C, 53·1; H, 6·4; N, 5·3. $C_{12}H_{17}O_4NS$ requires C, 53·1; H, 6·3; N, 5·2%).

Carboxymethyl 2-Nitroethyl Sulphide.—To a solution of thioglycollic acid (9·2 g.) and sodium methoxide (10·8 g.) in methyl alcohol (150 c.c.), 2-nitroethyl nitrate (13·6 g.) was added dropwise with stirring at 0—5°. After being stirred for 3 hours at 0—20° the mixture was filtered, treated with 2N-hydrochloric acid (50 c.c.), evaporated to dryness, and extracted with ether. Removal of the ether gave *carboxymethyl 2-nitroethyl sulphide* (9·9 g.) as a colourless syrup which solidified on standing, and crystallised from toluene, m. p. 47° (Found: C, 29·4; H, 4·0; N, 8·5. $C_4H_7O_4NS$ requires C, 29·1; H, 4·2; N, 8·5%).

Carboxymethyl 2-Nitroethyl Sulphone.—Oxidation of carboxymethyl 2-nitroethyl sulphide with hydrogen peroxide in boiling glacial acetic acid gave *carboxymethyl 2-nitroethyl sulphone* in almost quantitative yield. From alcohol–ether–light petroleum (b. p. 40—60°), white crystals, m. p. 115—116°, were obtained (Found: C, 24·7; H, 3·9; N, 7·1. $C_4H_7O_6NS$ requires C, 24·4; H, 3·6; N, 7·1%). The *ethyl* ester, prepared in almost quantitative yield by heating the acid in alcoholic solution, formed colourless crystals from alcohol, m. p. 62° (Found: C, 32·2; H, 4·8; N, 6·3. $C_6H_{11}O_6NS$ requires C, 32·0; H, 4·8; N, 6·2%).

Carboxymethyl 2-Aminoethyl Sulphide.—Carboxymethyl 2-nitroethyl sulphide (8·0 g.) in methyl alcohol (200 c.c.) was hydrogenated over Raney nickel at ordinary temperature and pressure. After filtration, removal of the methyl alcohol gave a nickel salt, which was dissolved in water and decomposed by hydrogen sulphide. The solution was filtered from nickel sulphide and evaporated to dryness. Crystallisation of the residue from alcohol gave *carboxymethyl 2-aminoethyl sulphide* (2·8 g.), m. p. 156° (Found: C, 35·3; H, 5·5; N, 10·6. $C_4H_9O_2NS$ requires C, 35·5; H, 6·6; N, 10·3%).

2-Nitroethyl Thiolacetate.—To a solution of thiolacetic acid (15·2 g.) and sodium methoxide (10·8 g.) in methyl alcohol (200 c.c.), 2-nitroethyl nitrate (27·2 g.) was added dropwise with stirring at 0—5°. After being stirred for 2 hours, the filtered solution was evaporated and distilled, giving *2-nitroethyl thiolacetate* (23·1 g.), b. p. 68—70°/0·1 mm. (Found: C, 32·0; H, 5·4; N, 9·4. $C_4H_7O_3NS$ requires C, 32·2; H, 4·7; N, 9·4%).

2-Nitroethylthiol.—(a) *From nitroethylene and hydrogen sulphide.* Nitroethylene (20 g.; Part I of this series) was added slowly with stirring to a saturated solution of hydrogen sulphide in alcohol (350 c.c.) at 0°. The vessel was then sealed and kept at 20° for 2 hours; some di-(2-nitroethyl) sulphide separated at this stage. After removal of the alcohol, distillation of the residue in nitrogen gave *2-nitroethylthiol* (5·2 g.) as a colourless liquid, b. p. 86—87°/14 mm. (Found: C, 22·4; H, 4·3; N, 12·9; S, 29·5. $C_2H_5O_2NS$ requires C, 22·4; H, 4·7; N, 13·1; S, 29·9%), and *di-(2-nitroethyl) sulphide* (11·8 g.) as a pale yellow oil, b. p. 140—144°/0·2 mm., which darkened on standing (Found: S, 17·8. $C_4H_8O_4N_2S$ requires S, 17·8%).

(b) *From 2-nitroethyl nitrate and potassium hydrogen sulphide.* 2-Nitroethyl nitrate (13·6 g.) was added dropwise with stirring to a solution of potassium hydrogen sulphide (7·2 g.) in methyl alcohol (100 c.c.) at room temperature. After being stirred for 3 hours, the mixture was filtered, evaporated to dryness, and extracted with ether. Distillation of the ethereal solution gave 2-nitroethylthiol (2·1 g.), b. p. 95°/20 mm.

(c) *By hydrolysis of 2-nitroethyl thiolacetate.* 2-Nitroethyl thiolacetate (7·4 g.) was kept for 1 hour at 20° with a solution of sodium hydroxide (4 g.) in water (70 c.c.). The solution was acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution, washed free of acetic acid with aqueous sodium hydrogen carbonate, was distilled in nitrogen, giving 2-nitroethylthiol (0·5 g.), b. p. 95—100°/20 mm. Mercury 2-nitrothioethoxide, prepared from the thiol and mercuric cyanide in alcohol, separated from alcohol in colourless needles, m. p. 67—68°. It decomposed rapidly on standing. *2 : 4-Dinitrophenyl 2-nitroethyl sulphide* was prepared by addition of 1-chloro-2 : 4-dinitrobenzene (1·1 g.) in alcohol (20 c.c.) to a solution of the thiol (0·6 g.) in N-sodium hydroxide (5·5 c.c.). The solution was heated to boiling and the product which separated crystallised from benzene, m. p. 196—197° (Found: N, 15·6. $C_8H_7O_6N_3S$ requires N, 15·4%).

Di-(2-nitroethyl) Sulphide.—2-Nitroethyl nitrate (27·2 g.) was added dropwise to a stirred solution of potassium sulphide (11·0 g.) in methyl alcohol (200 c.c.) at 0—5°. After being stirred for 2 hours, the filtered solution was evaporated to dryness, the residue extracted with acetone, and the extract distilled, yielding di-(2-nitroethyl) sulphide (9 g.) identical with that obtained from nitroethylene and hydrogen sulphide. Oxidation of the samples with hydrogen peroxide gave identical specimens of *di-(2-nitroethyl) sulphone*, colourless plates from acetone, m. p. 132° (Found: C, 22·6; H, 3·7; N, 13·2. $C_4H_8O_6N_2S$ requires C, 22·6; H, 3·8; N, 13·2%).

Nitro-tert.-butylthiol and Di(nitro-tert.-butyl) Sulphide.—(a) *From sodium sulphide.* 1-Nitro-2-methylprop-1-ene (101 g.) was added slowly to a stirred solution of sodium sulphide ($Na_2S,9H_2O$; 120 g.) in water (450 c.c.) at 0—10°. When homogeneous, the solution was treated with acetic acid (120 c.c. of 50%) and extracted with ether. Distillation afforded a fraction, b. p. 46—64°/7 mm. (38 g.), from which unchanged nitro-olefin was extracted with aqueous sodium hydrogen sulphite, giving *nitro-tert.-butylthiol* (12 g.), b. p. 58—63°/7 mm. (Found: C, 35·9; H, 6·3; N, 11·0; S, 22·9. $C_4H_9O_2NS$ requires C, 35·6; H, 6·7; N, 10·4; S, 23·7%). Mercury nitro-*tert.*-thiobutoxide, colourless needles from alcohol, m. p. 108°, decomposes slowly on keeping. The residue, after removal of the fraction, b. p. 46—64°/7 mm., was crystallised from benzene–light petroleum to give *di(nitro-tert.-butyl) sulphide*, m. p. 59—60° (Found: C, 40·8; H, 6·8; S, 13·5. $C_8H_{16}O_4N_2S$ requires C, 40·7; H, 6·8; S, 13·6%).

(b) *From hydrogen sulphide.* A solution of 1-nitro-2-methylprop-1-ene (20 g.) in alcohol (350 c.c.) was saturated at 0° with hydrogen sulphide and kept in a sealed vessel for 7 days at 20°. The alcohol was distilled and the residue, after extraction with aqueous sodium hydrogen sulphite, was isolated with ether and distilled giving nitro-*tert.*-butylthiol (8·4 g.), b. p. 68°/8 mm., and a residue (0·5 g.) which, after crystallisation from benzene-light petroleum, afforded di(nitro-*tert.*-butyl) sulphide, m. p. 59—60°.

Di(nitro-tert.-*butyl) Sulphone.*—Oxidation of di(nitro-*tert.*-butyl) sulphide with hydrogen peroxide in the manner described above gave *di(nitro*-tert.-*butyl) sulphone*, long colourless needles from methyl alcohol, m. p. 186° (Found : N, 10·4. $C_8H_{16}O_6N_2S$ requires N, 10·4%).

Di-(2-*nitro*-1-*methylpropyl*) *Sulphide.*—A solution of 2-nitrobut-2-ene (27·4 g.) in alcohol (350 c.c.) was saturated with hydrogen sulphide at 0°. The vessel was then sealed and kept at room temperature for 16 hours. After filtration and removal of the alcohol, distillation of the residue in a stream of nitrogen gave an almost colourless liquid, b. p. 70—90°/15 mm., and *di*-(2-*nitro*-1-*methylpropyl*) *sulphide* (3 g.), b. p. 110°/0·04 mm. (Found : S, 13·4. $C_8H_{16}O_4N_2S$ requires S, 13·6%). The fraction, b. p. 70—90°/15 mm., appeared to be a mixture of unchanged nitro-olefin and the stereoisomerides of 2-nitro-1-methylpropylthiol, but attempts to separate them by distillation failed. Redistillation of this material after 2 weeks, however, gave more (5 g.) di-(2-nitro-1-methylpropyl) sulphide, indicating reaction between the components.

Di-(2-*nitro*-1-*methylpropyl*) *Sulphone.*—Oxidation of the crude sulphide with hydrogen peroxide in the usual way gave a mixture of stereoisomerides of *di*-(2-*nitro*-1-*methylpropyl*) *sulphone* which separated from benzene–light petroleum (b. p. 60—80°) in colourless needles, m. p. 92—98° (Found : C, 35·8; H, 6·0; N, 10·2. $C_8H_{16}O_6N_2S$ requires C, 35·8; H, 6·0; N, 10·4%).

2-*Nitropropylthiol.*—2-Nitroprop-1-ene (20 g.) was added slowly with stirring to a saturated solution of hydrogen sulphide in alcohol (350 c.c.) at 0°. The vessel was then sealed and kept at 20° for 1½ hours. After removal of the alcohol, distillation of the residue gave 2-*nitropropylthiol* (2 g.) as a colourless liquid, b. p. 83°/12 mm. (Found : S, 25·8. $C_3H_7O_2NS$ requires S, 26·4%). The dark residue decomposed on attempted distillation at 0·2 mm.

Di-(2-*nitro*-1-*phenylethyl*) *Sulphide.*—A solution of β-nitrostyrene (30 g.) in alcohol (350 c.c.) was saturated with hydrogen sulphide at 0°. The vessel was then sealed and kept at 20° for 2 hours. On cooling to 0°, *di*-(2-*nitro*-1-*phenylethyl*) *sulphide* (9·5 g.) separated as a colourless solid which crystallised from alcohol in large prisms, m. p. 106—107° (Found : N, 8·3; S, 9·5. $C_{16}H_{16}O_4N_2S$ requires N, 8·4; S, 9·6%). The bulk of the product remained in the mother liquors as a viscous oil, b. p. 80—120°/0·08 mm.; this mixture of stereoisomerides was not separated.

p-*Tolyl* 2-*Nitroethyl Sulphone.*—(a) *From nitroethylene.* Nitroethylene (3·7 g.) was added slowly to a stirred solution of sodium *p*-toluenesulphinate (8·9 g.) in water (25 c.c.) at 0°. After being stirred at 0° for 3 hours, the mixture was filtered from polynitroethylene, acidified with acetic acid, and extracted with ether. Concentration of the ethereal solution gave p-*tolyl* 2-*nitroethyl sulphone* (0·6 g.) as colourless needles, m. p. 114° (from alcohol) (Found : C, 46·8; H, 5·0; N, 6·6. $C_9H_{11}O_4NS$ requires C, 47·2; H, 4·8; N, 6·1%).

(b) *From* 2-*nitroethyl nitrate and sodium* p-*toluenesulphinate.* 2-Nitroethyl nitrate (13·6 g.) was added dropwise to a stirred solution of sodium *p*-toluenesulphinate (17·8 g.) in water (50 c.c.) at 20°. The product was filtered off and crystallised from alcohol, giving *p*-tolyl 2-nitroethyl sulphone (18·3 g.), m. p. and mixed m. p. 114°.

(c) *From* p-*tolyl* 2-*nitroethyl sulphide.* A solution of sodium methoxide [from sodium (2·3 g.) in methyl alcohol (50 c.c.)] was added to a solution of thio-*p*-cresol (12·4 g.) in methyl alcohol (100 c.c.) at 0°. 2-Nitroethyl nitrate (13·6 g.) was then added dropwise with stirring at — 10° to — 5°. After being stirred for 3 hours the filtered solution was evaporated, giving crude *p*-tolyl 2-nitroethyl sulphide as a colourless oil, which on oxidation with hydrogen peroxide in acetic acid gave *p*-tolyl 2-nitroethyl sulphone (21 g.), m. p. and mixed m. p. 114°.

p-*Tolyl* 2-*Aminoethyl Sulphone.*—*p*-Tolyl 2-nitroethyl sulphone (2·3 g.) in methyl alcohol (40 c.c.) was hydrogenated over Raney nickel at ordinary temperature and pressure. Evaporation of the filtered solution gave *p*-tolyl 2-aminoethyl sulphone as a colourless syrup. The *benzoyl* derivative had m. p. 158° (Found : C, 63·2; H, 5·7; N, 4·7. $C_{16}H_{17}O_3NS$ requires C, 63·3; H, 5·6; N, 4·6%).

p-*Tolyl* 2-*Aminoethyl Sulphide.*—Crude *p*-tolyl 2-nitroethyl sulphide (5 g.) in methyl alcohol (50 c.c.) was hydrogenated over Raney nickel at ordinary temperature and pressure. Removal of the methyl alcohol gave a colourless syrup, which with ethereal hydrogen chloride yielded p-*tolyl* 2-*aminoethyl sulphide hydrochloride* (4·1 g.), colourless crystals from alcohol–ether, m. p. 132° (Found : C, 53·3: H, 6·9; N, 6·8. $C_9H_{13}NS,HCl$ requires C, 53·1; H, 6·9; N, 6·9%).

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284. *Aliphatic Nitro-compounds. Part V. Preparation of 2-Nitroalkanesulphonic Acids by Interaction of α-Nitro-olefins and Sodium Hydrogen Sulphite.**

By R. L. Heath and H. A. Piggott.

α-Nitro-olefins react with sodium hydrogen sulphite giving sodium 2-nitroalkanesulphonates, which on catalytic reduction afford the corresponding 2-aminoalkanesulphonic acids in good yield. In the absence of oxygen, sulphurous acid can be used in place of sodium hydrogen sulphite, and in many cases esters of 2-nitro-alcohols (2-nitroethyl nitrate, 2-nitropropyl acetate) behave in the same way as the nitro-olefins.

* Cf. E.P. 571,157.

THE interaction of α-nitro-olefins and sodium hydrogen sulphite was studied during a general investigation of the addition reactions of nitro-olefins, as a potentially interesting route to certain 2-aminoalkanesulphonic acids required as intermediates in the synthesis of dyestuffs.

The addition of alkali hydrogen sulphites to unsaturated substances has been studied by many workers. Rosenthal (*Annalen*, 1886, **233**, 38) prepared the diammonium salt of β-sulphopropionic acid by the interaction of ammonium hydrogen sulphite and ammonium acrylate. The addition of potassium hydrogen sulphite to allyl alcohol was demonstrated by Müller (*Ber.*, 1873, **6**, 1442), and the product was established by Marckwald (*ibid.*, 1898, **31**, 1864) as potassium 1-hydroxypropane-3-sulphonate. Kolker and Lapworth (*J.*, 1925, 307) added ammonium hydrogen sulphite to a large number of olefins, whilst the reaction of sodium hydrogen sulphite and styrene, first reported by Ashworth and Burkhardt (*J.*, 1928, 1791), has been shown by Kharasch, Schenck, and Mayo (*J. Amer. Chem. Soc.*, 1939, **61**, 3092) to yield 2-phenylethane-1-sulphonic acid, 2-phenylethylene-1-sulphonic acid, 2-phenylethane-1 : 1-disulphonic acid, and 2-hydroxy-2-phenylethane-1-sulphonic acid. Knoevenagel and Morrise (*Ber.*, 1904, **37**, 4038) successfully added alkali hydrogen sulphites to αβ-unsaturated aldehydes and ketones, and the addition to unsaturated furyl compounds has been described by the American Cyanamide Co. (Brit. Appl. 14357/43).

The formation of alkali 2-nitroalkanesulphonates by interaction of an α-nitro-olefin and alkali hydrogen sulphite was found to be a general reaction; in the absence of oxygen, sulphurous acid behaved in a similar way, giving the free nitro-sulphonic acid, but in the presence of oxygen sulphamic acid was formed, probably by (*a*) oxidation of sulphurous to sulphuric acid, (*b*) formation of hydroxylamine from sulphuric acid and the nitro-olefin, and (*c*) interaction of hydroxylamine and sulphur dioxide. The use of sodium sulphite in this reaction resulted in the formation of the sodium salt of the sodium *aci*-nitroalkanesulphonate, and in two cases esters of 2-nitro-alcohols have been shown to react in the same way as the nitro-olefins.

Accurate analyses of the nitroalkanesulphonates were not easy to obtain owing to the difficulty of freeing them from the last traces of moisture, and many were characterised as their *p*-toluidine salts (see Chambers and Watt, *J. Org. Chem.*, 1941, **6**, 376). All attempts to characterise them by salts of *S*-benzyl*iso*thiourea were unsuccessful.

The *sulphonates* which have been prepared are listed in the Table.

Nitro-compound.	Sulphite.	Nitro-sulphonate.
Nitroethylene	$NaHSO_3$	Na 2-nitroethanesulphonate
2-Nitroethyl nitrate	$NaHSO_3$	Na 2-nitroethanesulphonate
1-Nitroprop-1-ene	$NaHSO_3$	Na 1-nitropropane-2-sulphonate
1-Nitroprop-1-ene	H_2SO_3	1-Nitropropane-2-sulphonic acid
1-Nitroprop-1-ene	Na_2SO_3	Na_2 1-*aci*-nitropropane-2-sulphonate
2-Nitroprop-1-ene	$NaHSO_3$	Na 2-nitropropane-1-sulphonate
2-Nitropropyl acetate	$NaHSO_3$	Na 2-nitropropane-1-sulphonate
1-Nitro-2-methylprop-1-ene	$NaHSO_3$	Na 1-nitro-2-methylpropane-2-sulphonate
1-Nitro-2-methylprop-1-ene	H_2SO_3	1-Nitro-2-methylpropane-2-sulphonic acid
2-Nitrobut-2-ene	$NaHSO_3$	Na 2-nitrobutane-3-sulphonate and (?) Na 2-oximinobutane-3-sulphonate
2-Nitrostyrene	$NaHSO_3$	Na 1-nitro-2-phenylethane-2-sulphonate
2-Nitrostyrene	H_2SO_3	1-Nitro-2-phenylethane-2-sulphonic acid
1-Nitro-2-(2-furyl)ethylene	$NaHSO_3$	Na 1-nitro-2-(2-furyl)ethane-2-sulphonate
Ethyl α-nitro-ββ-dimethylacrylate	$NaHSO_3$	Na 1-nitro-1-carbethoxy-2-methylpropane-2-sulphonate

A few deviations from the normal reaction course were noted. 1-Nitro*cyclo*hexane and 2-nitro-1-phenylprop-1-ene with sodium hydrogen sulphite gave viscous syrups which could not be characterised and on reduction gave nitrogen-free products. 2-Nitrobut-2-ene, condensed with sodium hydrogen sulphite in an atmosphere of nitrogen, gave a syrupy and a crystalline condensation product both of which on reduction yielded amino-sulphonic acids which, whilst agreeing in analysis with the expected 2-aminobutanesulphonic acid, were not identical. The original crystalline product may be the oximino-sulphonic acid, but the structures of the amino-sulphonic acids have not been determined.

The interaction of ethyl α-nitro-ββ-dimethylacrylate and sodium hydrogen sulphite was described by Bouveault and Wahl (*Bull. Soc. chim.*, 1901, **25**, 910) who made no attempt to isolate or characterise the reaction product. This has been repeated and the product shown to be that of normal addition.

Reduction of the nitro-sulphonates with Raney nickel and hydrogen gave good yields of the corresponding amino-sulphonic acids: in most cases the reduction was sufficiently facile to

proceed at ordinary temperature and pressure and in only a few was it necessary to use hydrogen under pressure.

Experimental.

Analyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

Sodium 2-Nitroethanesulphonate.—(a) *From nitroethylene.* Nitroethylene (27·5 g.; this series, Part I) was added dropwise to a vigorously stirred solution of sodium hydrogen sulphite (39·2 g.) in water (70 c.c.) at − 5° to 0° and stirring continued at this temperature for 2 hours and finally at 20° for 4 hours. The mixture was evaporated under reduced pressure at 40° and the residue extracted with absolute alcohol, giving *sodium 2-nitroethanesulphonate* in 75% yield. The salt was recrystallised from alcohol (Found: N, 7·9. $C_2H_4O_5NSNa$ requires N, 7·9%). The *p-toluidine* salt, prepared by addition of aqueous *p*-toluidine hydrochloride to the aqueous sodium salt, formed needles from absolute alcohol, m. p. 179° (decomp.) (Found: C, 40·6; H, 5·5; N, 10·6. $C_2H_5O_5NS,C_7H_9N$ requires C, 41·2; H, 5·4; N, 10·7%).

(b) *From 2-nitroethyl nitrate.* 2-Nitroethyl nitrate (13·6 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) was added dropwise to a well-stirred solution of sodium hydrogen sulphite (20·8 g.) in water (40 c.c.) at − 5° to 0° and stirring was continued for 24 hours at 20°. 2-Nitroethyl nitrate (3·2 g.) was recovered from the solution by ether extraction, and the aqueous layer, after evaporation and extraction as described in (a) above, gave the nitro-sulphonic acid, characterised as its *p*-toluidine salt, in 50% yield.

2-Aminoethanesulphonic Acid.—The nitro-sulphonic acid (above) (1·77 g.) in water (30 c.c.) was shaken with hydrogen and Raney nickel at ordinary temperature and pressure. The filtered solution was evaporated to dryness, treated with concentrated hydrochloric acid, filtered, and again evaporated. The residue on crystallisation from aqueous alcohol afforded 2-aminoethanesulphonic acid (taurine), m. p. 317° (decomp.), in 65% yield. Cortese (*J. Amer. Chem. Soc.*, 1936, **58**, 191) gives m. p. 300—305° (decomp.) (Found: C, 19·2; H, 5·6; N, 10·9. Calc. for $C_2H_7O_3NS$: C, 19·2; H, 5·6; N, 11·2%).

Sodium 1-Nitropropane-2-sulphonate.—(a) *From sodium hydrogen sulphite.* The salt was prepared from 1-nitroprop-1-ene (17·4 g.; this series, Part I) and sodium hydrogen sulphite (20·8 g.) in water (50 c.c.) as described above for sodium 2-nitroethane sulphonate. *Sodium 1-nitropropane-2-sulphonate monohydrate* separated from alcohol in 78% yield (Found: C, 17·4; H, 4·1; N, 7·0. $C_3H_6O_5NSNa,H_2O$ requires C, 17·2; H, 3·8; N, 6·7%). The p-*toluidine* salt had m. p. 164—166° (Found: C, 43·8; H, 5·8; N, 10·2. $C_3H_7O_5NS,C_7H_9N$ requires C, 43·5; H, 5·8; N, 10·2%).

(b) *From sulphurous acid.* 1-Nitroprop-1-ene (10 g.) was shaken in a stoppered bottle at room temperature for 2 days with an aqueous solution of sulphurous acid (saturated at 0°). The solution was neutralised with sodium carbonate, evaporated to dryness at 40° under reduced pressure, and the residue extracted with hot absolute alcohol to give sodium 1-nitropropane-2-sulphonate, characterised as the *p*-toluidine salt, m. p. 164—166°.

(c) *From sodium sulphite.* 1-Nitroprop-1-ene (8·7 g.) was gradually added to a vigorously-stirred solution of sodium sulphite heptahydrate (25·2 g.) in water (25 c.c.) at 0—5° and stirring continued for a further 3 hours at 0—5° and at 20° for 16 hours. The solution was evaporated to dryness and the residue extracted with absolute alcohol to give *disodium* 1-aci-*nitropropane-2-sulphonate trihydrate*, which separated from aqueous alcohol in white crystals (Found: C, 13·6; H, 4·0; N, 5·3. $C_3H_5O_5NSNa_2,3H_2O$ requires C, 13·6; H, 4·1; N, 5·2%). It was characterised as its *p*-toluidine salt, m. p. 164—166° alone and in admixture with the sample prepared under (a) above.

1-Aminopropane-2-sulphonic Acid.—The nitro-sulphonic acid (above) was reduced with hydrogen and Raney nickel as described for 2-aminoethanesulphonic acid. The amino-acid, obtained in 79% yield, had m. p. 290—295° (decomp.) (Gabriel and Colman, *Ber.*, 1906, **39**, 2891, give m. p. 290—295°) (Found: C, 25·7; H, 6·5; N, 10·6. Calc. for $C_3H_9O_3NS$: C, 25·9; H, 6·5; N, 10·1%).

Sodium 2-Nitropropane-1-sulphonate.—(a) *From 2-nitroprop-1-ene.* This was prepared from 2-nitroprop-1-ene (this series, Part I) and sodium hydrogen sulphite as described for sodium 1-nitropropane-2-sulphonate. The salt was crystallised from absolute alcohol, giving *sodium 2-nitropropane-1-sulphonate* in 88% yield (Found: C, 18·7; H, 4·1; N, 7·0. $C_3H_6O_5NSNa$ requires C, 18·8; H, 3·1; N, 7·8%).

Catalytic reduction of the salt in the usual way afforded a 60% yield of 2-aminopropane-1-sulphonic acid, which separated from aqueous alcohol, m. p. 325—335° (decomp.); Gabriel and Ohle (*Ber.*, 1906, **39**, 2891) give m. p. 323° (decomp.) (Found: C, 25·9; H, 6·7; N, 10·0. Calc. for $C_3H_9O_3NS$: C, 25·9; H, 6·5; N, 10·1%).

(b) *From 2-nitropropyl acetate.* A mixture of 2-nitropropyl acetate (7·35 g.; Blomquist, Tapp, and Johnson, *J. Amer. Chem. Soc.*, 1945, **67**, 1519), sodium hydrogen sulphite (20·8 g.), and water (50 c.c.) was stirred vigorously at 35° for 16 hours. The homogeneous solution was evaporated to dryness and extracted with absolute alcohol. Evaporation of the alcohol gave a mixture of sodium acetate and sodium 2-nitropropane-1-sulphonate, which was reduced with hydrogen and nickel in the usual way, giving 2-aminopropane-1-sulphonic acid, m. p. 325—328° (decomp.).

Sodium 1-Nitro-2-methylpropane-2-sulphonate.—(a) *Using sodium hydrogen sulphite.* This reaction was carried out in the normal way using 1-nitro-2-methylprop-1-ene (Levy and Scaife, in the press) in place of the nitropropenes as described above. Recrystallisation from alcohol gave *sodium 1-nitro-2-methylpropane-2-sulphonate monohydrate* in 95% yield (Found: C, 22·3; H, 4·2; N, 6·1. $C_4H_8O_5NSNa,H_2O$ requires C, 21·5; H, 4·5; N, 6·3%).

(b) *Using sulphurous acid.* The nitro-olefin (10·1 g.) was shaken for 5 days at room temperature in a stoppered bottle with aqueous sulphurous acid (100 c.c. saturated at 0°) in an atmosphere of nitrogen. The solution was neutralised with sodium carbonate and worked up in the normal manner, giving sodium 1-nitro-2-methylpropane-2-sulphonate in 55% yield. In a parallel experiment in which the sulphurous acid solution had been prepared in the presence of air, the only isolated product was sulphamic acid, m. p. 212° (decomp.), obtained in 31% yield, identical with an authentic specimen (Found: H, 3·0; N, 14·3; S, 32·6. Calc. for H_3O_3NS: H, 3·1; N, 14·4; S, 33·0%).

1-*Amino*-2-*methylpropane*-2-*sulphonic Acid*.—The nitrosulphonic acid (above) (5 g.) in water (50 c.c.) was reduced with hydrogen and Raney nickel, and the product isolated as described for 2-aminoethanesulphonic acid. 2-*Amino*-2-*methylpropane*-2-*sulphonic acid* separated from aqueous alcohol as colourless crystals, m. p. 350—360° (decomp.), in 75% yield (Found: C, 31·0; H, 7·2; N, 8·8. $C_4H_{11}O_3NS$ requires C, 31·3; H, 7·2; N, 9·1%).

Sodium 2-*Nitrobutane*-3-*sulphonate*.—2-Nitrobut-2-ene (50·5 g.; this series, Part III) was added dropwise to a cooled solution of sodium hydrogen sulphite (52 g.) in water (120 c.c.). The reaction was carried out in an atmosphere of nitrogen, and stirring was continued for 16 hours. Unreacted 2-nitrobut-2-ene was removed by extraction with ether, the aqueous solution evaporated to dryness under reduced pressure, and the residue extracted with absolute alcohol from which, by evaporation, a pale yellow viscous syrup (80 g.) was obtained. A crystalline solid (10 g.) (see below) separated from this syrup on standing. The syrup, apparently crude sodium 2-nitrobutane-3-sulphonate, gave a *p-toluidine* salt which decomposed below its melting point (Found: C, 45·5; H, 5·8; N, 9·1. $C_4H_9O_5NS,C_7H_9N$ requires C, 45·5; H, 6·2; N, 9·6%). Reduction of the syrup with Raney nickel and hydrogen, followed by isolation in the usual way, gave 2-*aminobutane*-3-*sulphonic acid*, m. p. 267—270°, in 60% yield (Found: C, 31·3; H, 6·9; N, 9·5. $C_4H_{11}O_3NS$ requires C, 31·4; H, 7·2; N, 9·2%). The crystalline solid (above) could not be identified with certainty. It may be sodium 2-oximinobutane-3-sulphonate (Found: C, 24·7; H, 4·4; N, 7·4. Calc. for $C_4H_8O_4NSNa$: C, 25·4; H, 4·2; N, 7·4%). The *p*-toluidine salt had m. p. 186—188° (Found: C, 47·1; H, 6·6; N, 10·4. Calc. for $C_4H_9O_4NS,C_7H_9N$: C, 48·1; H, 6·6; N, 10·2%). On reduction with hydrogen and Raney nickel in the usual way it gave an amino-acid, m. p. 320—324° (decomp.), in 60% yield (Found: C, 30·6; H, 6·8; N, 9·0. Calc. for $C_4H_{11}O_3NS$: C, 31·4; H, 7·2; N, 9·2%).

2-*Nitro*-4-*methylpent*-2-*ene*.—To a cooled mixture of *iso*butaldehyde (36 g.) and diethylamine (10 g.), nitroethane (37·5 g.) was added during 30 minutes, the temperature being kept at 20—30° by intermittent cooling. The mixture was kept at 20° for 15 hours, acidified (2N-hydrochloric acid), extracted with ether, and the dried extract fractionated, giving 2-*nitro*-4-*methylpent*-2-*ene* (40·5 g.; 65%), b. p. 67°/10 mm., as a pale yellow lachrymatory oil (Found: C, 56·2; H, 8·1; N, 10·9. $C_6H_{11}O_2N$ requires C, 55·8; H, 8·5; N, 10·8%).

2-*Amino*-4-*methylpentane*-3-*sulphonic Acid*.—2-Nitro-4-methylpent-2-ene (12·9 g.) in methyl alcohol (35 c.c.) was added dropwise with stirring to a solution of sodium hydrogen sulphite (24 g.) in water (100 c.c.) and methyl alcohol (35 c.c.) at 20°. The mixture was maintained at 30° for 16 hours, evaporated, and extracted with hot absolute alcohol. Concentration of this extract yielded crude sodium 2-nitro-4-methylpentane-3-sulphonate as a pale yellow viscous syrup (yield, 99%), which could not be crystallised. Reduction in aqueous solution with Raney nickel and hydrogen at 25° and 100 atms. (initial pressure) gave 2-*amino*-4-*methylpentane*-3-*sulphonic acid*, white crystals from aqueous alcohol, decomp. > 340°, in 75% yield (Found: C, 40·0; H, 8·3; N, 7·7. $C_6H_{15}O_3NS$ requires C, 39·7; H, 8·3; N, 7·7%).

Sodium 1-*Nitro*-2-*phenylethane*-2-*sulphonate and* 1-*Amino*-2-*phenylethane*-2-*sulphonic Acid*.—(a) *From sodium hydrogen sulphite*. A solution of 2-nitrostyrene (14·9 g.) in dioxan (60 c.c.) was added slowly to a well-stirred solution of sodium hydrogen sulphite (15 g.) in water (90 c.c.) at 20°, and stirring then continued at 30° for 10 hours. Unchanged nitrostyrene was removed with ether, and the aqueous dioxan solution evaporated to dryness. The residue was crystallised from hot absolute alcohol, giving *sodium* 1-*nitro*-2-*phenylethane*-2-*sulphonate* as white crystals, unmolten at 300°, in 80% yield (Found: N, 5·2. $C_8H_8O_5NSNa$ requires N, 5·5%). Reduction in aqueous solution with Raney nickel and hydrogen at ordinary temperature and pressure, followed by working up in the normal way, afforded 1-*amino*-2-*phenylethane*-2-*sulphonic acid* in 70% yield, pearly plates from aqueous alcohol, m. p. 358—360° (decomp.) (Found: C, 47·1; H, 5·3; N, 7·0. $C_8H_{11}O_3NS$ requires C, 47·7; H, 5·5; N, 7·0%).

(b) *From sulphurous acid*. 2-Nitrostyrene (10 g.) was shaken with saturated aqueous sulphurous acid (100 c.c.) in a stoppered bottle in the absence of oxygen for 6 days at room temperature. The unreacted nitrostyrene (2·0 g.) was removed by filtration and the solution neutralised with solid sodium carbonate. The crude nitro-acid was reduced with Raney nickel and hydrogen, giving the amino-acid, m. p. 358—360° (decomp.), in 56% yield.

Sodium 1-*Nitro*-2-(2-*furyl*)*ethane*-2-*sulphonate*.—1-Nitro-2-(2-furyl)ethylene (13·9 g.; Thiele and Landers, *Annalen*, 1909, **369**, 303) in dioxan (50 c.c.) was slowly added to a stirred solution of sodium hydrogen sulphite (24 g.) in water (100 c.c.) and dioxan (50 c.c.) at 25°, and stirring continued for a further 16 hours. The solution was evaporated to dryness, and the residue, extracted with absolute alcohol, gave *sodium* 1-*nitro*-2-(2-*furyl*)*ethanesulphonate* as a colourless syrup which crystallised slowly on keeping, but could not be recrystallised (Found: C, 26·2; H, 4·2; N, 5·4. $C_6H_8O_6NSNa,2H_2O$ requires C, 25·8; H, 3·6; N, 5·0%). Reduction with Raney nickel and hydrogen in methyl alcohol at ordinary temperature and pressure gave 1-*amino*-2-(2-*furyl*)*ethane*-2-*sulphonic acid*, white crystals from aqueous dioxan, m. p. 250—252° (decomp.), in 30% yield (Found: N, 7·0. $C_6H_9O_4NS$ requires N, 7·3%).

1-*Amino*-1-*carbethoxy*-2-*methylpropane*-2-*sulphonic Acid*.—Ethyl α-nitro-ββ-dimethylacrylate (5 g.; Bouveault and Wahl, *Compt. rend.*, 1900, **131**, 687, 748) was added dropwise to a vigorously stirred solution of sodium hydrogen sulphite (5 g.) in water (20 c.c.) at 30°, and stirring was continued for a further 20 hours. The solution was evaporated under reduced pressure and extracted with hot absolute alcohol to give crude sodium 1-nitro-1-carbethoxy-2-methylpropane-2-sulphonate as a colourless glass in 84% yield. Reduction of the above salt (6·7 g.) in water (60 c.c.) with Raney nickel and hydrogen at ordinary temperature and 90 atms. (initial pressure), followed by evaporation of the filtered solution, afforded *sodium* 1-*amino*-1-*carbethoxy*-2-*methylpropanesulphonate*, white crystals from aqueous alcohol, in 45% yield (Found: N, 5·4. $C_7H_{14}O_5NSNa$ requires N, 5·7%). Acidification of an aqueous solution of the sodium salt with concentrated hydrochloric acid gave the free *amino-sulphonic acid*, white crystals from aqueous alcohol, m. p. 223°, in 34% yield (Found: N, 6·0. $C_7H_{15}O_5NS$ requires N, 6·2%).

Sodium 1-*Nitro*-2 : 4 : 4-*trimethylpentane*-2-*sulphonate*.—A mixture of 1-nitro-2 : 4 : 4-trimethylpent-1-ene (5 g.; see Levy, Scaife, and Baldock, in the press), dioxan (15 c.c.), and saturated aqueous sodium hydrogen sulphite (50 c.c.) was stirred at 20° for 8 hours. After concentration under reduced

pressure at 20°, the residual white solid was extracted with alcohol, filtered, and the extract treated with dry ether. A white crystalline salt was precipitated, and purified by reprecipitation from alcohol with ether. *Sodium 1-nitro-2 : 4 : 4-trimethylpentane-2-sulphonate* was obtained as white crystals, m. p. 189° (decomp.) (Found : N, 5·4; S, 12·8. $C_8H_{16}O_5NSNa$ requires N, 5·4; S, 12·3%).

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285. *Aliphatic Nitro-compounds. Part VI. Reaction of α-Nitro-olefins with Hydrochloric Acid.*

By ROYDEN L. HEATH and J. D. ROSE.

α-Nitro-olefins react with anhydrous hydrogen chloride in ether giving 1 : 2-dichloronitroso-compounds which rearrange, if an α-hydrogen atom is present, into 1 : 2-dichloro-oximes. These on hydrolysis with water afford hydroxylamine hydrochloride and an α-hydroxy- or α-chloro-carboxylic acid according to the extent of the hydrolysis. Reaction of the nitro-olefins containing an α-hydrogen atom with concentrated aqueous hydrochloric acid gives similar products, but the intermediate dichloro-oximes are not isolated. It is suggested that the initial step is a 1 : 4-addition of hydrogen chloride to the nitro-olefin.

THE literature on the action of hydrochloric acid on α-nitro-olefins is scanty. Haitinger (*Monatsh.*, 1881, **2**, 287; *Wien Akad. Ber.*, 1878, **77**, 428; *A*, 1879, 700) reported that 1-nitro-2-methylprop-1-ene, treated with hydrogen chloride at 20° or with boiling concentrated hydrochloric acid, gave hydroxylamine hydrochloride, carbon dioxide, and ammonia; a hydroxy-acid, m. p. 65°, was also isolated but not characterised. Our experience, below, suggests that this was probably impure α-hydroxy*iso*butyric acid (m. p. 79—80°). Priebs (*Annalen*, 1884, **225**, 319) obtained phenylchloroacetic acid by treatment of β-nitrostyrene with fuming hydrochloric acid at 100°.

A study of the action of hydrochloric acid on α-nitro-olefins was undertaken as part of a general exploration of the chemistry of the aliphatic nitro-compounds. In the case of nitro-olefins with an α-hydrogen atom ($R_2C{:}CH{\cdot}NO_2$), treatment with ethereal hydrogen chloride gave hydroxylamine hydrochloride and an α-chloro- or α-hydroxy-acid (cf. Priebs, *loc. cit.*).

The possibility that the first stage in the reaction was 1 : 2-addition of hydrogen chloride to the double bond was excluded when it was found that 2-nitro*iso*propyl chloride, $Me{\cdot}CHCl{\cdot}CH_2{\cdot}NO_2$, was not affected by ethereal hydrogen chloride under the conditions which converted 1-nitroprop-1-ene, $Me{\cdot}CH{:}CH{\cdot}NO_2$, into α-chloropropionic acid and hydroxylamine hydrochloride. It therefore follows that the first addition is 1 : 4- to give $R_2CCl{\cdot}CH{:}\overset{\nearrow O}{N}{\cdot}OH$, which, as the *aci*-form of a primary nitro-paraffin, breaks down *via* the hydroxamic acid to hydroxylamine hydrochloride and an α-chloro- or α-hydroxy-acid (depending on the lability of the chlorine atom). The mechanism of conversion of the *aci*-primary nitro-paraffin into hydroxamic acid is still obscure but is considered to involve the following steps (cf. Yale, *Chem. Reviews*, 1943, **33**, 226).

$$R{\cdot}CH_2{\cdot}NO_2 \longrightarrow R{\cdot}CH{:}\overset{\nearrow O}{N}{\cdot}OH \longrightarrow R{\cdot}CHCl{\cdot}\overset{\nearrow O}{N}H{\cdot}OH \xrightarrow{-H_2O} R{\cdot}CHCl{\cdot}NO$$

$$R{\cdot}CO_2H \longleftarrow R{\cdot}C(OH){:}N{\cdot}OH \longleftarrow R{\cdot}CCl{:}N{\cdot}OH$$

In this mechanism, an important stage is the rearrangement of the 1-chloronitroso-compound to an oxime, which requires a hydrogen atom on the carbon carrying the nitroso-group. From secondary nitro-paraffins, in which this hydrogen is not available, the product expected would therefore be a 1-chloronitroso-compound or its breakdown products. In agreement with this we have found that treatment of nitro-olefins of the type $RR'C{:}CR''{\cdot}NO_2$ with ethereal hydrochloric acid gives deep blue highly lachrymatory liquids. Although it has not been possible to obtain these analytically pure on account of the closeness of their boiling points to those of the parent nitro-olefins, there seems little doubt that these are the dichloronitroso-compounds.

$$RR'C{:}CR''{\cdot}NO_2 \xrightarrow{+HCl} \left[RR'CCl{\cdot}CR''{:}\overset{\nearrow O}{N}{\cdot}OH\right] \xrightarrow{+HCl} \left[RR'CCl{\cdot}CClR''{\cdot}\overset{\nearrow O}{N}H{\cdot}OH\right] \xrightarrow{-H_2O} RR'CCl{\cdot}CClR''{\cdot}NO$$

Attempts to break down these dichloronitroso-compounds by further treatment with hydrochloric acid gave a trace of hydroxylamine hydrochloride as the only product identified.

EXPERIMENTAL.

Action of Anhydrous Hydrogen Chloride on Nitroethylene.—Nitroethylene (37 g.; this series, Part I) was added dropwise to stirred saturated ethereal hydrogen chloride (300 c.c.) below 0°. Stirring was continued at 0° for 4 hours and at 20° for a further 12 hours. After removal of the ether under reduced pressure αβ-dichloroacetaldoxime remained as a colourless mobile liquid which began to decompose immediately. The crude product was stirred with water (300 c.c.) at 20° for 16 hours; the mixture, which was homogeneous, still gave a positive test for a hydroxamic acid and was refluxed for ½ hour (hydroxamic acid test negative) and evaporated to dryness under reduced pressure. The residue was extracted with ether, giving chloroacetic acid (39 g.; 82%), m. p. 62—63°, after recrystallisation from chloroform, and hydroxylamine hydrochloride (31·5 g.; 90%) as the ether-insoluble product.

Action of Concentrated Hydrochloric Acid on 2-Nitroethyl Alcohol.—2-Nitroethyl alcohol (10 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) was heated at 140° for 12 hours with concentrated hydrochloric acid (80 c.c.) in a sealed tube. The solution was evaporated and separated by ether into chloroacetic acid (6·2 g.; 60%) and hydroxylamine hydrochloride (5·3 g.; 70%).

Action of Anhydrous Hydrogen Chloride on 1-Nitroprop-1-ene.—This was carried out using 1-nitroprop-1-ene (51 g.; this series, Part I) and ethereal hydrogen chloride (250 c.c.) as described above for nitroethylene. The αβ-dichloropropaldoxime was distilled (80%), b. p. 78—80°/12 mm., but began to decompose immediately after distillation. A portion (37 g.) was hydrolysed by refluxing it with water (100 c.c.) for ½ hour. After evaporation the residue was separated by ether into lactic acid (8·0 g.; 33%), α-chloropropionic acid (0·7 g.; 2%), and hydroxylamine hydrochloride (10·4 g.; 60%).

Action of Concentrated Hydrochloric Acid on 1-Nitroprop-1-ene and 2-Nitroisopropyl Alcohol.—1-Nitroprop-1-ene (20 g.) was stirred with concentrated hydrochloric acid (100 c.c.) at 20° for 24 hours and then at 40° for 2 hours. After working up in the usual way, hydroxylamine hydrochloride (12 g.; 75%), lactic acid (6·0 g.; 30%), and α-chloropropionic acid (0·5 g.; 2%) were obtained. Similarly, 2-nitro*iso*propyl alcohol (10·5 g.) heated at 140° for 2 hours with concentrated hydrochloric acid (sealed tube) gave hydroxylamine hydrochloride (5·3 g.; 75%) and α-chloropropionic acid (5·6 g.; 54%).

Action of Anhydrous Hydrogen Chloride on 2-Nitroprop-1-ene.—2-Nitroprop-1-ene (26·1 g.; this series, Part I) was added dropwise with stirring to dry ether saturated at 0° with anhydrous hydrogen chloride (200 c.c.); a deep blue colour rapidly developed. Stirring was continued at 0° and precipitated hydroxylamine hydrochloride (1·8 g.) removed. Separated water was absorbed by the addition of anhydrous magnesium sulphate, and the solution distilled giving 1 : 2-dichloro-2-nitrosopropane, b. p. 48—50°/60 mm., as a deep blue, mobile, powerfully lachrymatory liquid (20 g.; 45%). It was not possible to obtain this material analytically pure owing to difficulties of separating small amounts of unchanged 2-nitroprop-1-ene (b. p. 45—48°/60 mm.).

Action of Anhydrous Hydrogen Chloride on 2-Nitrobut-2-ene.—2-Nitrobut-2-ene (20·2 g.; this series, Part III) was treated as described above for 2-nitroprop-1-ene. 2 : 3-Dichloro-2-nitrosobutane, b. p. 61—63°/40 mm., was obtained as a deep blue lachrymatory liquid (11 g.; 35%). After hydrolysis with water at 20° for 16 hours only hydroxylamine hydrochloride (0·1 g.) could be identified.

Action of Concentrated Hydrochloric Acid on 2-Nitrobut-2-ene.—2-Nitrobut-2-ene (20 g.) was stirred at 20° for 40 hours with concentrated hydrochloric acid (100 c.c.). The deep blue colour which developed initially disappeared in ½ hour. Evaporation to dryness under reduced pressure gave only hydroxylamine hydrochloride (7 g.; 52%).

Action of Anhydrous Hydrogen Chloride on 1-Nitro-2-methylprop-1-ene.—1-Nitro-2-methylprop-1-ene (60 g.; Levy and Scaife, in the press) was treated with saturated ethereal hydrogen chloride (400 c.c.) as described above for nitroethylene. αβ-Dichloro*iso*butaldoxime, b. p. 79°/10 mm., was obtained as a colourless liquid which began to decompose immediately after distillation (75 g.; 80%). Hydrolysis of this dichloro-oxime (24 g.) with boiling water (250 c.c.) for 16 hours gave hydroxylamine hydrochloride (9·5 g.; 90%) and α-hydroxy*iso*butyric acid, m. p. 80° (4·8 g.; 30%). Hydrolysis of the dichloro-oxime with concentrated hydrochloric acid for 1½ hours gave a 50% yield of α-hydroxy*iso*butyric acid.

Action of Concentrated Hydrochloric Acid on 1-Nitro-2-methylprop-1-ene.—1-Nitro-2-methylprop-1-ene (20·2 g.) was added dropwise with vigorous stirring to concentrated hydrochloric acid (100 c.c.) at 15—20°. Stirring was continued for 16 hours, and the mixture then boiled for 15 minutes and worked up in the usual way, giving hydroxylamine hydrochloride (12 g.; 86%) and α-hydroxy*iso*butyric acid (11·3 g.; 54%).

Action of Anhydrous Hydrogen Chloride on 1-Nitro-2-chloropropane.—1-Nitro-2-chloropropane (Henry, *Bull. Soc. chim.*, 1895, **13**, 1000) was treated with anhydrous ethereal hydrogen chloride under the conditions described for 1-nitroprop-1-ene (see above). On distillation unchanged 1-nitro-2-chloropropane, b. p. 60—65°/14 mm., was recovered quantitatively.

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286. *Aliphatic Nitro-compounds. Part VII. Preparation of 2-Nitroalkylamines.*

By R. L. HEATH and J. D. ROSE.

Ammonia and primary or secondary amines interact with α-nitro-olefins, giving 2-nitroalkylamines. Those formed from ammonia or aliphatic amines are in general extremely unstable, but can be reduced by nickel and hydrogen to derivatives of ethylenediamine. *N*-2-Nitroalkylarylamines formed from aromatic amines are somewhat more stable, but are best isolated and characterised through their salts. In many cases 2-nitroethyl nitrate can be

used as a convenient laboratory substitute for nitroethylene, and 2-nitro*iso*propyl acetate or 2-nitro*iso*propyl nitrate can replace 1-nitroprop-1-ene.

THE addition of ammonia and amines to α-nitro-olefins has hitherto received only scant attention in the literature. The reaction of nitroethylene with aniline (Wieland and Sakellarios, *Ber.*, 1919, **52**, 898) and nuclear substituted anilines (Kodak Ltd., B.P. 539,070; 21.2.40) is known to give *N*-2-nitroethylanilines, but in most cases the products were not characterised and experimental details are lacking. β-Nitrostyrene reacts with hydroxylamine to give $Ph{\cdot}CH(NH{\cdot}OH){\cdot}CH_2{\cdot}NO_2$ (Posner, *Annalen*, 1912, **389**, 114), but the reaction with other bases is erratic. Worrall (*J. Amer. Chem. Soc.*, 1927, **49**, 1598) attempted to add some forty bases (amines, hydrazines) to β-nitrostyrene and found that only thirteen gave isolatable adducts. Aniline and *p*-toluidine were the only common aromatic bases and piperidine the only secondary amine with which he was able to obtain an adduct, and in each of these three cases the adduct was of type (I).

$$R_2C{:}CR{\cdot}NO_2 + R_2NH \longrightarrow \underset{\text{(I.)}}{R_2C(NR_2){\cdot}CHR{\cdot}NO_2} \xrightarrow{H} \underset{\text{(II.)}}{R_2C(NR_2){\cdot}CHR{\cdot}NH_2}$$

The addition of ammonia was, however, exceptional, two mols. of β-nitrostyrene being involved to give $NH(CHPh{\cdot}CH_2{\cdot}NO_2)_2$.

Halogen-substituted nitro-olefins have also been reported to react with amines. Thus β-bromo-β-nitrostyrene with ammonia gives 2-bromo-2-nitro-1-phenylethylamine (Loevenich and Gerber, *Ber.*, 1930, **63**, 1707), and 1-bromo-1-nitrobut-1-ene with aliphatic amines gives unstable adducts (Loevenich, Koch, and Pucknat, *Ber.*, 1930, **63**, 636).

A study of the addition of amines to nitro-olefins has now been undertaken as part of a general investigation of the aliphatic nitro-compounds and as a possible route to certain substituted derivatives of ethylenediamine required for other work.

The addition of ammonia and amines to nitro-olefins is a general reaction which in most cases proceeds very readily. The yields are variable, but this is due to the instability of the resulting 2-nitroalkylamine in which the basic group causes rapid decomposition of the primary or secondary nitro-compound. The products from aromatic amines are weaker bases than those from ammonia or aliphatic amines and are therefore more stable, but in both series it was found preferable to isolate the adducts as salts. Hydrogenation of the 2-nitroalkylamines to ethylenediamines was carried out using Raney nickel.

A complication in carrying out these additions was the tendency of the nitro-olefins to polymerise under the influence of the amine. It was found that better yields of some adducts were obtained when esters of the corresponding 2-nitro-alcohols were used in place of the nitro-olefin. Thus 2-nitroethyl nitrate and 2-nitro*iso*propyl acetate could be used to replace nitroethylene and 1-nitroprop-1-ene, respectively.

Ammonia has been caused to react with 2-nitroethyl nitrate, 1-nitroprop-1-ene, 2-nitrobut-2-ene, and 1-nitro-2-methylprop-1-ene to give the corresponding unstable β-nitro-amines (type I) which were characterised as salts. Hydrogenation of the nitro-amines over Raney nickel gave the 1 : 2-diamines (type II). Similarly, diethylamine reacted with 2-nitroethyl nitrate and 2-nitrobut-2-ene to give nitro-amines (type I). From 1 : 2 : 3 : 4-tetrahydroquinoline, the N-2-*nitroethyl* derivative was obtained in 75% yield from 2-nitroethyl nitrate, but in only 12·5% yield from nitroethylene itself.

Aniline has been caused to react with nitroethylene, 2-nitroethyl nitrate, 1-nitroprop-1-ene, and 2-nitrobut-2-ene; *N*-methylaniline with nitroethylene, 1-nitroprop-1-ene, and 2-nitro*iso*propyl acetate; *N*-ethylaniline with nitroethylene, 2-nitroethyl nitrate, and 1-nitroprop-1-ene. All the products were of type I and readily reverted to nitro-olefin and amine on treatment with alkali (which polymerised the nitro-olefin formed), and in some cases dilute acid affected the same fission. A bis-adduct, *di-(2-nitroethyl)aniline*, was isolated as its *hydrochloride* after further reaction of *N*-2-nitroethylaniline with nitroethylene; this salt eliminated nitroethylene on being heated in water. There was evidence that 2-nitroethylaniline reacted with 1-nitroprop-1-ene, but the product was too unstable for isolation.

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton. M. ps. are uncorrected.

2-Nitroethylamine and Ethylenediamine.—2-Nitroethyl nitrate (13·6 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) was added dropwise with stirring to methyl alcohol (200 c.c.) saturated with dry ammonia at − 5°, and stirring continued for 4 hours at − 5° to 0°. The mixture was filtered and the filtrate evaporated at 40° under reduced pressure to give a light brown oil (9 g.). The crude 2-nitro-

ethylamine could not be distilled, did not give a crystalline hydrochloride or picrate, and decomposed to a black tar in 1 to 2 hours. The crude product (8 g.) in methyl alcohol (300 c.c.) was shaken with hydrogen and Raney nickel at ordinary temperature and pressure; the hydrogen absorption was almost theoretical. The mixture was filtered, acidified with hydrochloric acid, and evaporated to dryness; the semi-solid crystalline mass was intimately mixed with powdered potassium hydroxide and dry distilled to give an aqueous solution of ethylenediamine (5·4 g.), b. p. 100—110°; the dipicrate, m. p. 232—234° (decomp.), was identical with an authentic specimen.

2-*Nitroiso*propylamine.—1-Nitroprop-1-ene (30 g.; this series, Part I) was added with stirring to methyl-alcoholic ammonia (200 c.c.) at 0° and stirring continued for 3 hours The solution was evaporated and distilled, giving 2-nitro*iso*propylamine, b. p. 50—55°/10 mm. Yield, 55%. 2-Nitro-*iso*propylamine is very unstable and decomposes in 24 hours. The *hydrochloride* had m. p. 114° (Found: C, 26·0; H, 6·4; Cl, 25·5. $C_3H_8O_2N_2$,HCl requires C, 25·6; H, 6·4; Cl, 25·3%).

1 : 2-*Diaminopropane*.—The nitroamine (above) (10 g.) in methyl alcohol (400 c.c.) was shaken with hydrogen in the presence of Raney nickel at ordinary temperature and pressure. The theoretical amount of hydrogen was absorbed. The solution was filtered, acidified with concentrated hydrochloric acid, and evaporated to dryness at 40° under reduced pressure to give 1 : 2-diaminopropane dihydrochloride which crystallised in long needles from alcohol–ether, m. p. 221° (Strache, *Ber.*, 1888, **21**, 2359, gives m. p. 220°). Yield, 52%. The dipicrate formed yellow needles from water, m. p. 237° (Windaus, Dorries, and Jensen, *Ber.*, 1921, **54**, 2750, give m. p. 237°).

Di-(2-*nitroisopropyl*)*amine*.—Dry ammonia was passed for 1 hour through a solution of 2-nitro-*iso*propyl nitrate (30 g.; Levy and Scaife, *J.*, 1946, 1100) in dry ether (200 c.c.). The solution, filtered from ammonium nitrate (15·7 g.), was fractionated, giving *di*-(2-*nitroisopropyl*)*amine*, b. p. 60—62°/0·5 mm. Yield, 12·7 g. (Found: N, 21·6. $C_6H_{13}O_4N_3$ requires N, 22·0%).

2-*Nitro*-3-*aminobutane*.—2-Nitrobut-2-ene (20·2 g.; this series, Part III) was added dropwise with stirring to methyl-alcoholic ammonia (250 c.c.) at 0° and stirring continued for 2 hours. The solution was evaporated and distilled, giving 2-nitro-3-aminobutane as an almost colourless liquid, b. p. 75—78°/20 mm., $n_D^{18°}$ 1·4720 (60%), which decomposed in 2 days. The *hydrochloride*, m. p. 115° (decomp.), was also unstable (Found: Cl, 23·4. $C_4H_{10}O_2N_2$,HCl requires Cl, 23·0%).

2 : 3-*Diaminobutane*.—2-Nitro-3-aminobutane (6 g.) in methyl alcohol (60 c.c.) was shaken with hydrogen in the presence of Raney nickel. When absorption was complete the solution was filtered, acidified with hydrochloric acid, evaporated to dryness, and the crystalline residue of the *dihydrochloride* recrystallised from aqueous alcohol to m. p. 312°. Yield, 40% (Found: C, 29·8; H, 8·2; N, 17·4. $C_4H_{12}N_2$,2HCl requires C, 29·8; H, 8·7; N, 17·4%). Angeli (*Ber.*, 1890, **23**, 1357) reports that the dihydrochloride of 2 : 3-diaminobutane is crystalline, but gives no m. p. The picrate decomposed at 250—253° (Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, 1924, **43**, 309T, give m. p. 250—252°).

1-*Nitro*-2-*amino*-2-*methylpropane*.—Dry ammonia was passed into a solution of 1-nitro-2-methylprop-1-ene (Levy and Scaife, in the press) in dry benzene (100 c.c.) at 20° for 8 hours, and the solution then distilled giving 1-nitro-2-amino-2-methylpropane as an oil, b. p. 62—65°/11 mm., in 40% yield. The nitroamine was unstable and decomposed in 3—4 days. The *hydrochloride*, from absolute alcohol, had m. p. 182° (decomp.) (Found: N, 18·1; Cl, 22·9. $C_4H_{10}O_2N_2$,HCl requires N, 18·1; Cl, 23·0%). Reduction of the nitroamine with Raney nickel and hydrogen afforded 1 : 2-diamino-2-methylpropane isolated in 75% yield as the dihydrochloride, m. p. 302°. Strack and Schwaneberg (*Ber.*, 1933, **66**, 1333) give m. p. 303° (Found: Cl, 44·2. Calc. for $C_4H_{12}N_2$,2HCl: Cl, 44·1%).

Diethyl-2-*nitroethylamine*.—2-Nitroethyl nitrate (6·8 g.) was added dropwise with stirring to diethylamine (7·3 g.) in dry ether (100 c.c.) kept at 0° by external cooling. After the addition was complete, stirring was continued for ½ hour. The solution was filtered and the ether removed at 20° under reduced pressure. An attempt to distil a small portion of the residue at 15 mm. was unsuccessful; the product decomposed violently. The *hydrochloride*, from alcohol–ether, had m. p. 72—75° (Found: Cl, 19·3. $C_6H_{14}O_2N_2$,HCl requires Cl, 19·4%). The *picrate* formed needles from alcohol, m. p. 88° (Found: C, 38·6; H, 4·8; N, 18·4. $C_6H_{14}O_2N_2$,$C_6H_3O_7N_3$ requires C, 38·2; H, 5·0; N, 18·5%).

2-*Nitro*-3-*diethylaminobutane*.—2-Nitrobut-2-ene (10·1 g.) in dry ether (10 c.c.) was added dropwise with stirring to diethylamine (7·3 g.) in dry ether (25 c.c.) at 0—10° and the mixture stirred for a further 2 hours. The product was fractionated to give 2-nitro-3-diethylaminobutane, b. p. 90—95°/11 mm., in 65% yield. Much decomposition had occurred after 12 hours. The *picrolonate* had m. p. 267° (decomp.) (Found: C, 49·4; H, 5·4. $C_{18}H_{26}O_7N_6$ requires C, 49·3; H, 5·9%).

N-(2-*Nitroethyl*)-1 : 2 : 3 : 4-*tetrahydroquinoline*.—(a) *From 2-nitroethyl nitrate*. 2-Nitroethyl nitrate (5·9 g.) was added dropwise with stirring to tetrahydroquinoline (11·8 g.), the temperature being kept below 30°. After 1 hours' stirring the product was dissolved in ether (50 c.c.) and washed with water. Ethereal hydrogen chloride was added to the dried ethereal solution and the precipitated *hydrochloride* crystallised from absolute alcohol, m. p. 132°. Yield, 75% (Found: N, 11·4; Cl, 14·3. $C_{11}H_{14}O_2N_2$,HCl requires N, 11·5; Cl, 14·6%).

(b) *From nitroethylene*. A mixture of equimolecular amounts of nitroethylene and tetrahydroquinoline stirred at 40° for 1 hour gave the base, isolated as the hydrochloride, m. p. 132°, in 12·5% yield.

2-*Nitroethylaniline*.—(a) *From nitroethylene*. The base was prepared according to Wieland and Sakellarios (*Ber.*, 1919, **52**, 898). Yield, 80%; m. p. 37°.

(b) *From 2-nitroethyl nitrate*. To a well-stirred solution of aniline (37·2 g.) in ether (250 c.c.), 2-nitroethyl nitrate (27·2 g.) was added dropwise at room temperature. After being stirred for 2 hours the ethereal solution was washed with water, dried, and concentrated under reduced pressure below 30°. The resulting syrup crystallised on cooling strongly, and separated from ether–light petroleum in golden plates, m. p. 37° (22 g.; 65%). The *hydrochloride* formed needles from alcohol–ether, m. p. 109° (Found: N, 13·9. $C_8H_{10}O_2N_2$,HCl requires N, 13·8%). The *acetyl* derivative formed long needles from aqueous alcohol, m. p. 99° (Found: N, 13·2. $C_{10}H_{12}O_3N_2$ requires N, 13·4%).

Di-(2-*nitroethyl*)*aniline*.—Nitroethylene (3·7 g.) was added with stirring to 2-nitroethylaniline (8·3 g.) at 0—10°. After 2 hours the product was dissolved in a mixture of acetone (50 c.c.) and ether (50 c.c.), and ethereal hydrogen chloride added. The precipitated *hydrochloride* separated from dry alcohol

containing hydrogen chloride as prisms, m. p. 128° (7·8 g.; 50%) (Found: Cl, 12·7. $C_{10}H_{13}O_4N_3$,HCl requires Cl, 12·9%). The free *base*, m. p. 64°, was obtained by crystallising the hydrochloride from aqueous alcohol (Found: C, 50·0; H, 5·7; N, 17·0. $C_{10}H_{13}O_4N_3$ requires C, 50·2; H, 5·4; N, 17·5%).

Methyl-2-nitroethylaniline.—Nitroethylene (3·6 g.) was added dropwise with stirring to methylaniline (5·3 g.) at 0—10° and the reaction completed by heating at 40° for 1 hour; the product distilled at 110°/0·2 mm. (yield, 4·5 g.; 50%). The *hydrochloride* had m. p. 82° (Found: N, 12·4; Cl, 16·5. $C_9H_{12}O_2N_2$,HCl requires N, 12·9; Cl, 16·4%).

Ethyl-2-nitroethylaniline.—(a) *From 2-nitroethyl nitrate.* The preparation was carried out from ethylaniline and 2-nitroethyl nitrate as described under (b) above for the preparation of 2-nitroethylaniline. The product was isolated in 80% yield as the *hydrochloride*, m. p. 114° (Found: N, 12·2; Cl, 15·3. $C_{10}H_{14}O_2N_2$,HCl requires N, 12·2; Cl, 15·4%). The free base was formed by gradual addition of solid sodium carbonate (6·6 g.) to a fine suspension of the hydrochloride (30 g.) in water (100 c.c.) at 0—5°. *Ethyl-2-nitroethylaniline* separated as a pale green oil which was isolated by ether and distilled, b. p. 108°/0·1 mm., $n_D^{19°}$ 1·5597. Yield, 70% (Found: C, 61·8; H, 7·2; N, 14·4. $C_{10}H_{14}O_2N_2$ requires C, 61·8; H, 7·2; N, 14·4%). The *picrate*, from alcohol, had m. p. 106° (Found: C, 45·9; H, 4·5; N, 16·3. $C_{10}H_{14}O_2N_2$,$C_6H_3O_7N_3$ requires C, 45·4; H, 4·0; N, 16·5%).

(b) *From nitroethylene.* The preparation was carried out as described above for the preparation of methyl-2-nitroethylaniline, and the hydrochloride, m. p. 114°, isolated in 75% yield.

2-Nitroisopropylaniline.—This was prepared from 1-nitroprop-1-ene (8·7 g.) and aniline (9·3 g.) in ether (100 c.c.) at room temperature for 2 hours. Removal of the ether under reduced pressure gave a yellow oil which solidified on cooling to − 50°, and was crystallised from alcohol, giving yellow needles of *2-nitroisopropylaniline*, m. p. 33° (Found: C, 60·05; H, 6·45; N, 15·2. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·6; N, 15·5%). The hydrochloride, from 2N-hydrochloric acid, had m. p. 148° (Found: N, 12·8; Cl, 16·6. Calc. for $C_9H_{12}O_2N_2$,HCl: N, 12·9; Cl, 16·4%). Fourneau (*Bull. Soc. chim.*, 1944, **11**, 143) gives m. p. 141°.

Methyl-2-nitroisopropylaniline.—(a) *From 1-nitroprop-1-ene.* Methylaniline (53·5 g.) was added dropwise to well stirred 1-nitroprop-1-ene (43 g.), the temperature being kept below 30° by external cooling. The crude product was dissolved in ether (500 c.c.) and added slowly with stirring to cool ethereal hydrogen chloride (500 c.c. containing 20 g. of hydrogen chloride). The separated solid was triturated twice with methyl alcohol–ether (1 : 2), giving the pure *hydrochloride* (106 g.; 92%), m. p. 126° (Found: Cl, 15·5. $C_{10}H_{14}O_2N_2$,HCl requires Cl, 15·3%). The hydrochloride, which is largely hydrolysed in aqueous solution, was treated in water with sodium carbonate, giving a pale green oil, which was isolated with ether and distilled, yielding *methyl-2-nitroisopropylaniline*, b. p. 112—115°/0·5 mm., in 80% yield (Found: C, 62·3; H, 7·2. $C_{10}H_{14}O_2N_2$ requires C, 61·8; H, 7·2%). The *picrate* had m. p. 116° (Found: C, 45·3; H, 4·3; N, 16·8. $C_{10}H_{14}O_2N_2$,$C_6H_3O_7N_3$ requires C, 45·4; H, 4·0; N, 16·6%). The *perchlorate* formed colourless prisms from alcohol–ether, m. p. 116° (Found: C, 40·3; H, 5·1; N, 9·4. $C_{10}H_{14}O_2N_2$,$HClO_4$ requires C, 40·7; H, 5·1; N, 9·5%). The *hydrochloride* of the p-*nitroso*-derivative, prepared by nitrosation of the hydrochloride, formed dark green crystals from methyl alcohol, and decomposed at 160° (Found: C, 46·4; H, 5·2. $C_{10}H_{13}O_3N_3$,HCl requires C, 46·2; H, 5·4%).

(b) *From 2-nitroisopropyl acetate.* A mixture of methylaniline (5·3 g.) and 2-nitro*iso*propyl acetate (7·4 g.; Schmidt and Rutz, *Ber.*, 1928, **61**, 2142) was heated at 50° for 8 hours. The crude product was converted into the hydrochloride, m. p. 126°, which was obtained in 50% yield.

Ethyl-2-nitroisopropylaniline.—This was prepared from 1-nitroprop-1-ene and ethylaniline as described for methyl 2-nitroethylaniline above. The *hydrochloride*, from alcohol, had m. p. 123°. Yield, 90% (Found: C, 54·1; H, 6·7; N, 11·3. $C_{11}H_{16}O_2N_2$HCl requires C, 53·9; H, 6·9; N, 11·4%).

Ethyl-2-nitro-n-propylaniline.—This was prepared from 2-nitroprop-1-ene (58 g.) and ethylaniline (80 g.) in ether (250 c.c.) as described for the isomeride above. It was isolated as the *hydrochloride*, m. p. 126°, in 50% yield (Found: C, 54·1; H, 6·9; N, 11·3. $C_{11}H_{16}O_2N_2$,HCl requires C, 53·9; H, 6·9; N, 11·4%).

2-Nitro-1-methyl-n-propylaniline.—2-Nitrobut-2-ene (24 g.) was added dropwise with stirring to aniline (18·6 g.) at 20°, the mixture maintained at 30° for 3 hours, and distilled, giving the base, b. p. 86°/0·5 mm., $n_D^{17°}$ 1·5570, in 72% yield. The *hydrochloride*, from methyl alcohol–ether, had m. p. 122° (Found: C, 52·4; H, 6·5; N, 12·0. $C_{10}H_{14}O_2N_2$,HCl requires C, 52·1; H, 6·5; N, 12·1%). The *perchlorate* explodes on warming (Found: C, 41·1; H, 5·2; N, 9·4. $C_{10}H_{14}O_2N_2$,$HClO_4$ requires C, 40·7; H, 5·1; N, 9·5%).

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287. *Aliphatic Nitro-compounds. Part VIII. Addition of Primary and Secondary Nitro-paraffins to α-Nitro-olefins to give* 1 : 3-*Dinitro-paraffins.**

By A. LAMBERT and H. A. PIGGOTT.

Interaction of primary or secondary aliphatic nitro-compounds with α-nitro-olefins yields 1 : 3-dinitro-paraffins, which on reduction afford 1 : 3-diamines. The reaction appears to be a general one, but yields are variable. An attempted condensation of 2 : 4-*dinitro*-2 : 3-*dimethylpentane* with formaldehyde gave, surprisingly, *methyl 2-nitro*-1 : 2-*dimethylpropyl ketoxime*.

* Patent application pending.

MANY authors have described the addition of nitro-paraffins to activated ethylenic systems, including αβ-unsaturated ketones (Kohler, *J. Amer. Chem. Soc.*, 1916, **38**, 889, and later papers), unsaturated esters (Kohler and Engelbrecht, *ibid.*, 1919, **41**, 764), and nitriles (Bruson, *ibid.*, 1943, **65**, 23), but little attention has been paid to their addition to the α-nitro-olefins. Worrall (*ibid.*, 1935, **57**, 2299; cf. Heim, *Ber.*, 1911, **44**, 2016) recorded the interaction of α-nitrostilbene and phenylnitromethane in the presence of ammonia to give 1 : 3-dinitro-1 : 2 : 3-triphenylpropane, and since the present work was completed, Hass (*Ind. Eng. Chem.*, 1943, **35**, 1151) has mentioned the formation of 1 : 3-dinitro-2 : 3-dimethylpropane from nitromethane and 1-nitro-2-methylpropene, but in neither case was experimental detail presented.

A systematic investigation of the addition of nitro-paraffins to nitro-olefins was undertaken as part of a general exploration of the addition reactions of the nitro-olefins and as a possible route to a wide variety of substituted 1 : 3-diamines of interest in connection with other work in these laboratories. The addition of a primary or secondary nitro-paraffin to a nitro-olefin, although a general reaction, afforded the 1 : 3-dinitro-paraffins in extremely variable yields.

$$\underset{\text{(I.)}}{CHRR'\cdot NO_2} + CHR''{:}CR'''\cdot NO_2 \longrightarrow \underset{\text{(II.)}}{CRR'(NO_2)\cdot CHR''\cdot CHR'''\cdot NO_2}$$

Thus, 2-nitrobut-2-ene (I, R″ = R‴ = CH_3) and 2-nitropropane in presence of sodium ethoxide yielded 47% of 2 : 4-*dinitro*-2 : 3-*dimethylpentane* (II, R = R′ = R″ = R‴ = Me); in this case the nitro-olefin is not easily polymerised by alkali, the product, containing only one active hydrogen atom, does not easily interact further with unchanged nitro-olefin, and the amount of polymeric by-product was therefore negligible. In the presence of benzyltrimethylammonium hydroxide, nitroethane and 2-nitrobut-2-ene gave the disecondary nitro-paraffin, 2 : 4-*dinitro*-3-*methylpentane*, in 28% yield with a considerable amount of by-product of high molecular weight which decomposed on attempted distillation; with sodium ethoxide or piperidine as catalyst the same product was obtained in lower yield. 2-Nitropropane and 2-nitroprop-1-ene gave (sodium ethoxide catalyst) 2 : 4-*dinitro*-2-*methylpentane* in 26% yield, and methyl 2-nitropropyl sulphide and methyl 2-nitropropyl ether (see Parts IV and III in this series) added (sodium methoxide catalyst) to 2-nitroprop-1-ene to give *methyl* 2 : 4-*dinitro*-2-*methylamyl sulphide* and *methyl* 2 : 4-*dinitro*-2-*methylamyl ether*, respectively; the latter was also obtained directly in 52% yield from two molecules of 2-nitroprop-1-ene and one of sodium methoxide without isolation of the intermediate methyl 2-nitropropyl ether. The higher nitro-olefins were less reactive; thus, 2-nitropropane and 1-nitro*cyclo*hexene gave *nitro*-2-(1-*nitro*iso*propyl*)-cyclo*hexane* in only 16% yield.

The properties of the 1 : 3-dinitro-paraffins are parallel to those of the simpler mononitro-compounds; they exhibit none of the instability associated with the 1 : 2-dinitro-paraffins. Hydrogenation in the presence of nickel catalysts affords 1 : 3-diamines; they dissolve in aqueous alkali and treatment of such solutions with bromine gives the α-bromo-derivatives which are useful for characterisation purposes. Surprising results were obtained in an attempt to cause 2 : 4-dinitro-2 : 3-dimethylpentane to interact with paraformaldehyde and sodium hydroxide; instead of the expected 4-hydroxymethyl derivative, *methyl 2-nitro*-1 : 2-*dimethylpropyl ketoxime*, m. p. 51°, was formed. This is the only known example of the reduction of a secondary nitro-paraffin by formaldehyde and alkali; the structure of the oxime was confirmed by reduction of the sodium salt of the dinitro-compound with stannous chloride and hydrochloric acid, a method specific for the reduction of primary or secondary nitro-paraffins to oximes (cf. Konowalov, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 960; *Chem. Zentr.*, 1899, I, 597). In addition to the oxime, m. p. 51°, above, the *isomeride*, m. p. 85—86°, was also formed, which was rearranged with phosphorus pentachloride to an isomeric *amide*.

The 2-nitroprop-1-ene used in this work was prepared by the method of Buckley and Scaife (this series, Part I).

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton. M. ps. are uncorrected.

2 : 4-*Dinitro*-2 : 3-*dimethylpentane*.—A well-stirred solution of sodium ethoxide (39·6 g.) in alcohol (400 c.c.) was treated with 2-nitropropane (52·5 g.) at 15—20°, followed by 2-nitrobut-2-ene (59·5 g.; this series, Part III), and the whole refluxed. After cooling, the mixture was poured into iced water (1000 c.c.) and neutralised at 0° with 2N-hydrochloric acid. The solution was concentrated under reduced pressure and the residue extracted with ether. Distillation gave 2 : 4-*dinitro*-2 : 3-*dimethylpentane* (53 g.) as a pale yellow oil, b. p. 90—92°/0·5 mm. (Found : C, 44·9; H, 7·5; N, 14·5. $C_7H_{14}O_4N_2$ requires C, 44·2; H, 7·4; N, 14·7%). The 2-*bromo*-derivative, prepared from an aqueous solution of sodium 2 : 4-dinitro-2 : 3-dimethylpentane and the calculated quantity of bromine, formed colourless plates from methyl alcohol, m. p. 40° (Found : C, 30·8; H, 4·7; N, 10·3; Br, 29·7. $C_7H_{13}O_4N_2Br$

requires C, 31·2; H, 4·8; N, 10·4; Br, 29·7%). The 2-(p-*nitrophenylazo*)-derivative, prepared from sodium 2 : 4-dinitro-2 : 3-dimethylpentane and diazotised *p*-nitroaniline (cf. Feasley and Degering, *J. Org. Chem.*, 1943, **8**, 12), formed orange prisms from alcohol, m. p. 142—143° (Found : C, 46·2; H, 5·1; N, 20·7. $C_{13}H_{17}O_6N_5$ requires C, 46·0; H, 5·0; N, 20·6%).

2 : 4-*Diamino*-2 : 3-*dimethylpentane*.—2 : 4-Dinitro-2 : 3-dimethylpentane (50 g.) in methyl alcohol was hydrogenated at 50—70° and 70 atms. (initial pressure) over Raney nickel. Fractionation of the product gave 2 : 4-diamino-2 : 3-dimethylpentane (17 g.) as a colourless liquid, b. p. 66—68°/30 mm., 180°/754 mm. Reduction with iron and hydrochloric acid gave the same diamine in poor yield. The NN'-*dibenzoyl* derivative formed colourless needles from benzene, m. p. 175° (Found : C, 74·5; H, 7·4; N, 8·2. $C_{21}H_{26}O_2N_2$ requires C, 74·6; H, 7·7; N, 8·3%). The *platinichloride* formed orange prisms from aqueous alcohol (Found : Pt, 36·1. $C_7H_{18}N_2,H_2PtCl_6$ requires Pt, 36·1%).

Methyl 2-*Nitro*-1 : 2-*dimethylpropyl Ketoxime*.—(a) *By reduction with formaldehyde*. 2 : 4-Dinitro-2 : 3-dimethylpentane (10 g.), paraformaldehyde (1·6 g.), 40% aqueous sodium hydroxide (0·5 c.c.), and methyl alcohol (20 c.c.) were stirred at room temperature for 16 hours. After neutralisation with dilute hydrochloric acid, fractionation gave a colourless oil (8·2 g.), b. p. 90—91°/<0·5 mm., which slowly deposited crystalline material. *Methyl* 2-*nitro*-1 : 2-*dimethylpropyl ketoxime* separated from light petroleum (b. p. 60—80°) as colourless plates, m. p. 51° (Found : C, 47·9; H, 8·1; N, 15·9. $C_7H_{14}O_3N_2$ requires C, 48·2; H, 8·0; N, 16·1%). The p-*nitrophenylurethane* formed fibrous needles from benzene–light petroleum (b. p. 60—80°), m. p. 109—110° (after being dried at 80° in a vacuum) (Found : C, 49·7; H, 5·2; N, 16·3. $C_{14}H_{19}O_6N_4$ requires C, 49·7; H, 5·3; N, 16·6%).

(b) *By reduction with stannous chloride*. A solution of 2 : 4-dinitro-2 : 3-dimethylpentane (30 g.) in aqueous sodium hydroxide (12·6%; 50 c.c.) was added dropwise with stirring to a solution of stannous chloride (35 g.) in concentrated hydrochloric acid (210 c.c.) at 0°. After being stirred for a further ½ hour at 0°, the solution was neutralised with sodium carbonate and extracted with ether. Distillation of the extract gave a viscous pale yellow oil (7 g.), b. p. 80—90°/0·1 mm., which crystallised on standing, m. p. and mixed m. p. with the oxime described above, 51°. The *p*-nitrophenylurethane had m. p. 109—110° alone or mixed with the specimen described above. The product from a second similar experiment was crystallised without distillation, giving an isomeric *oxime*, small needles from light petroleum (b. p. 60—80°), m. p. 85—86° (Found : C, 48·5; H, 8·1; N, 15·8. $C_7H_{14}O_3N_2$ requires C, 48·2; H, 8·0; N, 16·1%). With phosphorus pentachloride in dry ether the latter gave an isomeric *amide* which separated from benzene–light petroleum (b. p. 60—80°) in colourless needles, m. p. 83° (Found : C, 47·8; H, 8·2; N, 15·7. $C_7H_{14}O_3N_2$ requires C, 48·2; H, 8·0; N, 16·1%).

2 : 4-*Dinitro*-3-*methylpentane*.—2-Nitrobut-2-ene (50 g.) was added during 1 hour with stirring at ordinary temperature to a mixture of nitroethane (150 g.), dioxan (150 c.c.), and aqueous benzyltrimethylammonium hydroxide (40%; 6 c.c.). After being stirred for 48 hours at 40°, the mixture was diluted with water (500 c.c.) and neutralised with dilute hydrochloric acid. Extraction with ether, followed by fractionation, gave 2 : 4-*dinitro*-3-*methylpentane* (25 g.) as a pale yellow liquid, b. p. 94—95°/0·5 mm. (Found : N, 15·9. $C_6H_{12}O_4N_2$ requires N, 16·2%). The use of piperidine or sodium ethoxide as catalyst in this reaction gave a smaller yield of the same product. The 2 : 4-*dibromo*-derivative, prepared by the method described above from 2-bromo-2 : 4-dinitro-2 : 3-dimethylpentane, formed colourless prisms from aqueous methyl alcohol, m. p. 53—54° (Found : C, 21·7; H, 3·3; N, 8·0. $C_6H_{10}O_4N_2Br_2$ requires C, 21·6; H, 3·0; N, 8·3%).

2 : 4-*Dinitro*-2-*methylpentane*.—2-Nitropropane (21 g.) was added to 2-nitroprop-1-ene (20 g.; this series, Part I) as described above for the reaction of 2-nitropropane with 2-nitrobut-2-ene. 2 : 4-*Dinitro*-2-*methylpentane* (10·6 g.) was obtained as a pale yellow oil, b. p. 80°/0·2 mm. (Found : C, 41·3; H, 6·7. $C_6H_{12}O_4N_2$ requires C, 40·9; H, 6·8%). The 2-*bromo*-derivative formed colourless leaflets from aqueous methyl alcohol, m. p. 76° (Found : C, 27·7; H, 4·5; Br, 31·3. $C_6H_{11}O_4N_2Br$ requires C, 28·2; H, 4·3; Br, 31·4%).

2 : 4-*Diamino*-2-*methylpentane*.—2 : 4-Dinitro-2-methylpentane (9 g.) in methyl alcohol (100 c.c.) was hydrogenated at 70° and 75 atm. (initial pressure) over Raney nickel. The product was filtered, acidified with hydrochloric acid, evaporated to dryness, treated with excess of 50% aqueous potassium hydroxide, and extracted with ether. After drying over potassium hydroxide, distillation gave 2 : 4-diamino-2-methylpentane as a colourless liquid which fumed on exposure to air, b. p. 150—155°/756 mm. (Kohn, *Monatsh.*, 1902, **23**, 6, gives b. p. 147—155°). The NN'-*dibenzoyl* derivative formed colourless prisms from aqueous methyl alcohol, m. p. 152° (Found : N, 8·6. $C_{20}H_{24}O_2N_2$ requires N, 8·6%).

Nitro-2-(1-*nitroisopropyl*)cyclo*hexane*.—2-Nitropropane (8·9 g.) was brought into reaction with nitro*cyclo*hexene (12·7 g.) (Wieland *et al.*, *Annalen*, 1921, **424**, 71) as described above for the addition of 2-nitropropane to 2-nitrobut-2-ene. Fractionation of the product gave a pale yellow oil (3·5 g.), b. p. 95—110°/0·3 mm., which solidified on cooling, and recrystallised from light petroleum (b. p. 60—80°), giving *nitro*-2-(1-*nitroisopropyl*)cyclo*hexane* in colourless plates, m. p. 103° (Found : C, 49·9; H, 7·3; N, 12·6. $C_9H_{16}O_4N_2$ requires C, 50·0; H, 7·4; N, 13·0%).

Methyl 2 : 4-*Dinitro*-2-*methylamyl Ether*.—(a) *From methyl* 2-*nitropropyl ether and* 2-*nitroprop*-1-*ene*. A well-stirred solution of sodium methoxide (4·1 g.) in methyl alcohol (50 c.c.) was treated with methyl 2-nitropropyl ether (9·1 g.; this series, Part III), followed by 2-nitroprop-1-ene (6·6 g.) at room temperature. After being stirred at 40—50° for ½ hour, the mixture was poured into iced water (100 c.c.) and neutralised with aqueous acetic acid. The alcohol was distilled under reduced pressure and the residue extracted with ether. Distillation of the ethereal solution gave *methyl* 2 : 4-*dinitro*-2-*methylamyl ether* (8·0 g.) as a pale yellow oil, b. p. 92—94°/0·1 mm. (Found : C, 41·2; H, 6·8; N, 13·1. $C_7H_{14}O_5N_2$ requires C, 40·8; H, 6·8; N, 13·6%). The 4-*bromo*-derivative formed colourless plates from aqueous methyl alcohol, m. p. 64° (Found : C, 29·6; H, 4·8; N, 9·5; Br, 27·9. $C_7H_{13}O_5N_2Br$ requires C, 29·5; H, 4·6; N, 9·8; Br, 28·1%).

(b) *From* 2-*nitroprop*-1-*ene and methyl alcohol*. 2-Nitroprop-1-ene (50 g.) was added dropwise with stirring to a solution of sodium methoxide (15·5 g.) in methyl alcohol (200 c.c.) at 0°. After being stirred at room temperature for ½ hour, the mixture was poured into ice–water (500 c.c.), neutralised with aqueous acetic acid, and extracted with ether. Distillation of the ethereal solution gave *methyl*

2 : 4-*dinitro*-2-*methylamyl ether* (35 g.), b. p. 94—96°/0·2 mm. The 4-*bromo*-derivative had m. p. 64°, alone or mixed with the specimen described above.

Methyl **2 : 4-*Diamino*-2-*methylamyl Ether*.**—The dinitro-ether (above) (41·6 g.) in methyl alcohol (650 c.c.) was hydrogenated at 60—70° and 87 atms. (initial pressure). Fractionation of the product gave *methyl* **2 : 4-*diamino*-2-*methylamyl ether*** (20 g.) as a colourless liquid, b. p. 77—79°/10 mm. (Found: N, 18·7. $C_7H_{18}ON_2$ requires N, 19·2%). The *bis*-**2 : 4-*dinitrophenylurea*** derivative (cf. McVeigh and Rose, *J.*, 1945, 621) had m. p. 190° (Found: C, 44·7; H, 4·5; N, 19·8. $C_{21}H_{24}O_{11}N_8$ requires C, 44·6; H, 4·3; N, 19·9%).

Methyl **2 : 4-*Dinitro*-2-*methylamyl Sulphide*.**—Methyl 2-nitropropyl sulphide (19·6 g.; this series, Part IV) was brought into reaction with 2-nitroprop-1-ene (12·7 g.) as described above for the addition of 2-nitroprop-1-ene to methyl 2-nitropropyl ether. *Methyl* **2 : 4-*dinitro*-2-*methylamyl sulphide*** (10 g.) was obtained as a pale yellow oil, b. p. 110—115°/0·05 mm. (Found: N, 12·1; S, 14·3. $C_7H_{14}O_4N_2S$ requires N, 12·6; S, 14·4%).

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288. *Aliphatic Nitro-compounds. Part IX. Reaction of Nitro-paraffins with Ethylmagnesium Bromide.*

By G. D. BUCKLEY.

In the reaction of nitroethane with ethylmagnesium bromide the first stage is addition of the Grignard reagent to the N=O bond to form a complex (III) which on reduction with zinc and hydrochloric acid gives diethylamine. The complex may react with a second mol. of ethylmagnesium bromide with evolution of 1 mol. of ethane to form a new complex which yields *NN*-diethylhydroxylamine on hydrolysis. Nitromethane, 2-nitropropane, and 2-nitro-2-methylpropane form analogous complexes.

THE action of Grignard reagents on nitro-paraffins was first examined by Moureu (*Compt. rend.*, 1901, **132**, 837), who observed that nitroethane reacted with 2 mols. of ethylmagnesium iodide to form *NN*-diethylhydroxylamine. He suggested that the reaction involved the direct addition of both mols. of Grignard reagent to the N=O bonds, followed by breakdown on hydrolysis:

$$2MgEtI + Et\cdot NO_2 \longrightarrow Et_2N\langle^{O\cdot MgI}_{O\cdot MgI} \xrightarrow{H_2O} Et_2N\langle^{OH}_{OH} \longrightarrow Et_2N\cdot OH + EtOH$$

(I.)

Bevad (*Ber.*, 1907, **40**, 3065) studied the reactions of primary and secondary nitro-paraffins with several alkyl-zinc and -magnesium iodides. He found that nitroethane reacted with ethylmagnesium iodide with evolution of ethane and a little ethylene to give a complex which on hydrolysis gave *NN*-diethylhydroxylamine accompanied by smaller amounts of diethylamine and ethyl-*sec.*-butylhydroxylamine. Ethylzinc iodide reacted in a similar manner, but gave ethyl-*sec.*-butylhydroxylamine as the main product. Similar results were obtained with 1- and 2-nitropropanes. As the first stage in the reaction, Bevad postulated reaction of the Grignard reagent with the *aci*-form of the nitro-paraffin to give the complex (II), followed by addition of one or two mols. of Grignard reagent to the double bonds:

(II.) $CH_3\cdot CH{=}N\langle^{O\cdot MgI}_{O}$ $\qquad$ $CH_3\cdot CH_2\cdot N(O\cdot MgBr)\rightarrow O$ (III.)
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_2H_5$

It was later shown by Zerewitinoff (*Ber.*, 1910, **43**, 3593) that primary and secondary nitro-paraffins reacted with methylmagnesium iodide to give slightly less than 1 equivalent of methane, and he also considered that this arose from reaction with the *aci*-nitro-paraffin. Finally Wang (*Trans. Sci. Soc. China*, 1933, **7**, 253) made a detailed study of the products obtained by the action of excess of phenylmagnesium bromide on nitromethane. The chief products were phenylmethylhydroxylamine, phenylbenzylhydroxylamine, phenol, and benzene, and a mechanism was formulated, differing in detail from Bevad's theory, but also based on the preliminary formation of a complex of type (II).

All the theories so far advanced are inadmissible since they involve quinquecovalent nitrogen; a complex of type (I) as advocated by Moureu would be expected to yield a trialkylamine oxide and not a dialkylhydroxylamine on hydrolysis. The theories advanced by subsequent authors all postulate the preliminary tautomeric change of the nitro-compound to the *aci*-form, though no evidence has been adduced for the occurrence of this change, which normally requires strongly ionising conditions.

The reaction has therefore been re-examined, particular attention being directed to the initial stages. Treatment of nitroethane with 1 mol. of ethylmagnesium bromide at 0° resulted in a vigorous exothermic reaction to form a solid complex which separated from the solution. No gas was evolved during this reaction, but on addition of a further 2 mols. of Grignard reagent the complex largely redissolved and 1 mol. of gas was evolved; this reaction was relatively slow and required heating to drive it to completion. The gas was not identified, but was assumed to be mainly ethane on the evidence of Bevad (*loc. cit.*). The unreacted Grignard reagent, estimated by treating the mixture with water and collecting the evolved gas, amounted to 1 mol. The main liquid product was diethylhydroxylamine. The initial complex was shown by analysis to be an addition product of equimols. of nitroethane and ethylmagnesium bromide, and on reduction with zinc and hydrochloric acid it gave diethylamine in 60% yield. It must therefore have the structure (III). The analogous complex from nitromethane gave methylethylamine on reduction. Similar addition products were obtained by the action of ethylmagnesium bromide on 2-nitropropane and 2-nitro-2-methylpropane, but attempts to reduce them with zinc and hydrochloric acid failed owing to their instability.

It is evident from these results that the first step in the reaction of a nitro-paraffin with ethylmagnesium bromide is the addition of the Grignard reagent to the N=O bond to form a complex of type (III), which is then reduced by a second mol. of Grignard reagent, by a mechanism which is still obscure, to a product which on hydrolysis yields the dialkylhydroxylamine.

Experimental.

The nitro-paraffins used were purified by repeated distillation over phosphoric oxide, followed by thorough washing with water, drying ($CaCl_2$), and fractionation through a Widmer column. An ethereal solution of ethylmagnesium bromide was filtered through glass wool; the ethylmagnesium bromide content was determined by the method of Gilman *et al.* (*J. Amer. Chem. Soc.*, 1923, **45**, 150), and the solution was then diluted with dry ether to a concentration of 2 g.-mols. per l.

Nitroethane.—(*a*) A solution of nitroethane (7·5 g.) in pure dry ether (25 c.c.) was placed in a flask cooled in ice–salt and fitted with a mercury-sealed stirrer, reflux condenser, dropping funnel, and system for collecting evolved gases. Ethylmagnesium bromide solution (50 c.c.) was added dropwise to the stirred solution during 1 hour at − 5° to 0°. A strongly exothermic reaction took place and a heavy white precipitate was formed, but no gas was evolved. A further 100 c.c. of the Grignard solution was added during 1 hour, by which time the precipitate had largely redissolved and 1400 c.c. of gas had been evolved. The mixture was then refluxed for 1 hour (resulting in the evolution of a further 800 c.c. of gas), cooled in ice, and treated with water (50 c.c.) dropwise at 0—10°. During the addition of the water, 2200 c.c. of gas were evolved.

(*b*) Ethylmagnesium bromide solution (50 c.c.) was added dropwise during 1 hour to a stirred solution of nitroethane (7·5 g.) in pure dry ether (100 c.c.) at − 5° to 0°. The mixture was then refluxed for 1 hour; no gas was evolved. After cooling, the precipitate was collected, washed with pure dry ether, and dried in a vacuum at 20°, giving a hygroscopic white powder (17·4 g.) which appeared to decompose on treatment with water (Found: Br, 37·25; Mg, 11·65. $C_4H_{10}O_2NBrMg$ requires Br, 38·45; Mg, 11·54%).

This *complex* (15 g.) was dissolved in 19% hydrochloric acid (200 c.c.) with ice-cooling, and granulated zinc (30 g.) was added. The reduction was completed by heating on the steam-bath for a short time and the mixture was then cooled in ice, basified with excess of 32% sodium hydroxide solution, and steam-distilled into N-hydrochloric acid (100 c.c.); back-titration of the distillate with N-sodium hydroxide showed that base equivalent to 45·3 c.c. of N-acid (60% theory) had distilled. The neutralised solution was evaporated to dryness and the crude hydrochloride treated with concentrated sodium hydroxide solution. The base, which separated as a volatile oil, reacted with picryl chloride to give a picramide, m. p. 164—165°, not depressed on admixture with diethyl picramide, m. p. 165° (Found: N, 19·8. Calc. for $C_{10}H_{13}O_8N_4$: N, 19·7%). With phenyl *iso*cyanate the base gave a urea, m. p. 83—84°, not depressed on admixture with *N'*-phenyl-*NN*-diethylurea, m. p. 84°.

(*c*) Ethylmagnesium bromide solution (750 c.c.) was added during 2 hours to a stirred solution of nitroethane (37·5 g.) in dry ether (100 c.c.) at 0—10°. The mixture was refluxed for 4 hours, cooled, poured into ice, and steam-distilled until the distillate was only faintly alkaline to brilliant-yellow paper. The distillate was acidified with hydrochloric acid, and the ethereal layer was separated, washed with water, and discarded. The combined aqueous layer and washings were concentrated under reduced pressure, cooled, treated with a large excess of sodium hydroxide, and extracted with ether. The extract was dried (KOH) and fractionated to give diethylhydroxylamine as a colourless oil (20·4 g.), b. p. 50—52°/18 mm. (Found: equiv., 88·3. Calc. for $C_4H_{11}ON$: equiv., 89), together with small amounts of a volatile base, probably diethylamine, and a high-boiling residue which was not further examined.

Nitromethane.—Nitromethane (6·1 g.) was brought into reaction with ethylmagnesium bromide solution (50 c.c.) by the method (*b*) described above for nitroethane. This gave the *complex* (14·5 g.) as a hygroscopic white powder (Found: Br, 41·75; Mg, 12·65. $C_3H_8O_2NBrMg$ requires Br, 41·25; Mg, 12·4%). Reduction with zinc and hydrochloric acid gave methylethylamine (63% yield), characterised as the picrate, m. p. 96°, and the hydrobromide, m. p. 87—88° (Found: Br, 57·2. Calc. for C_3H_9N,HBr: Br, 57·15%).

2-*Nitropropane.*—2-Nitropropane (8·9 g.) was brought into reaction with ethylmagnesium bromide solution (50 c.c.) by the method (*b*) described above for nitroethane to give the *complex* (17·2 g.) as a

hygroscopic white powder (Found: Br, 35·3; Mg, 10·65. $C_8H_{12}O_2NBrMg$ requires Br, 36·05; Mg, 10·8%).

Nitro-tert.-*butane*.—Nitro-*tert*.-butane (10·3 g.) was brought into reaction with ethylmagnesium bromide solution (50 c.c.) by the method (*b*) described above for nitroethane. This gave a hygroscopic white *complex* (10 g.) (Found: Br, 34·2; Mg, 10·3. $C_6H_{14}O_2NBrMg$ requires Br, 33·9; Mg, 10·15%).

The author wishes to thank Dr. H. A. Piggott and Mr. J. D. Rose for advice and encouragement during this work.

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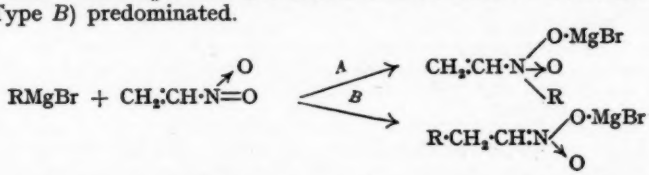
289. *Aliphatic Nitro-compounds. Part X. Action of Grignard Reagents on the α-Nitro-olefins.*

By G. D. BUCKLEY.

The reactions of ethyl- and butyl-magnesium bromides with two primary and one secondary α-nitro-olefins have been studied, and, although most of the reaction products have been identified, several points in the mechanism remain obscure. The initial step is a rapid 1 : 4-addition of the Grignard reagent to the conjugated system C:C·N:O to give a complex which may be decomposed by water to give a nitro-paraffin, or may react with more Grignard reagent to give another complex which on treatment with water yields an oxime. Simultaneously, some 1 : 2-addition to the nitro-olefin occurs, to give a complex which with water gives basic products, probably dialkylhydroxylamines.

ALTHOUGH organo-magnesium halides readily add to the N=O bond of the nitro-group (see Part IX of this series), Kohler and Stone (*J. Amer. Chem. Soc.*, 1930, **52**, 761) have shown that α-nitrostilbene and triphenylnitroethylene react with organo-magnesium halides to give exclusively 1 : 4-addition products. It was therefore of interest to study the reaction of Grignard compounds with aliphatic nitro-olefins to find whether 1 : 2-addition (Type *A*) or 1 : 4-addition (Type *B*) predominated.



Addition of ethylmagnesium bromide to an ethereal solution of nitroethylene resulted in immediate polymerisation of the nitro-olefin, but, by reversing the procedure, polymerisation was completely prevented. Slow addition of nitroethylene to 3 mols. of ethylmagnesium bromide at 10—15° resulted in a slow evolution of gas, which was accelerated on boiling the mixture. When 0·66 mol. of gas had been evolved, reaction appeared to be complete, and on treatment of the mixture with water a further 0·75 mol. of gas was evolved, presumably from unreacted Grignard reagent. The acid-insoluble part of the product consisted essentially of two substances, (*a*) 1-nitrobutane (20% yield) identified by its nitrolic acid reaction (Meyer, *Annalen*, 1875, **175**, 120) and by its degradation to *n*-butaldehyde, and (*b*) hexan-3-one oxime (30% yield) which was readily converted into the corresponding 2 : 4-dinitrophenylhydrazone (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2995) and was also reduced to 3-aminohexane. The acid-soluble part of the product was small and boiled over a wide range. It reduced ammoniacal silver nitrate and was hydrogenated to a mixture of non-reducing bases, but no identifiable substance was isolated either before or after hydrogenation. These properties indicated presence of a hydroxylamine.

Nitroethylene reacted similarly with excess of *n*-butylmagnesium bromide to give a 43% yield of 1-nitrohexane, a 27·5% yield of a neutral oil, $C_{10}H_{21}ON$, and a small amount of reducing bases. The compound, $C_{10}H_{21}ON$, was assumed to be *decan-5-one oxime* from its reactions and by analogy with the previous example. It was converted into an oily 2 : 4-dinitrophenylhydrazone which, in agreement with the failure of Bried and Hennion (*J. Amer. Chem. Soc.*, 1938, **60**, 1718) to prepare crystalline derivatives of decan-5-one, could not be obtained solid; catalytic reduction gave *5-aminodecane*.

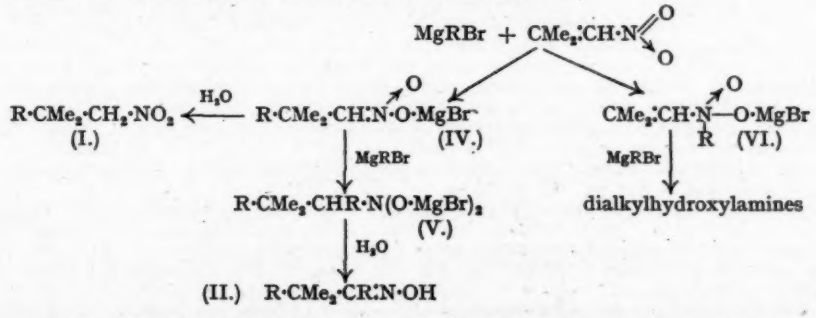
Since 1-nitro-2-methylprop-1-ene is not polymerised by Grignard reagents, it was possible to

* Cf. B.P. 571,804.

study more closely the course of the reaction of ethylmagnesium bromide with this nitro-olefin. This reaction of the first mol. of Grignard reagent was strongly exothermic and took place readily at 0° without evolution of gas. Further Grignard reagent reacted only slowly at 0°, but more readily at 15—20°. The reaction was mildly exothermic, and 1 mol. of gas was evolved, 3 mols. of Grignard reagent being consumed in all. The gas had the properties of a saturated hydrocarbon, and on combustion was found to be chiefly ethane. The products were 1-*nitro*-2 : 2-*dimethylbutane* (20%) (which gave the characteristic primary nitro-compound reaction and on reduction afforded the known 1-amino-2 : 2-dimethylbutane), and a crystalline solid, $C_8H_{17}ON$ (28%), which failed to react with 2 : 4-dinitrophenylhydrazine or 2 : 4-dinitrophenylsemicarbazide and was hydrogenated only with difficulty to a primary amine, $C_8H_{19}N$; by analogy with the previous examples it is believed to be 3 : 3-*dimethylhexan*-4-*one oxime* (II; R = Et), and the derived amine, 4-*amino*-3 : 3-*dimethylhexane*, the unreactivity of the oxime being attributed to steric factors.

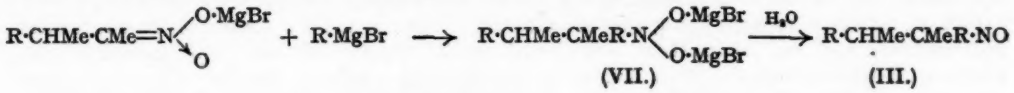
Addition of ethylmagnesium bromide to 2-nitrobut-2-ene gave polymers as in the case of nitroethylene, but this was again overcome by adding the nitro-olefin to excess of the Grignard reagent. Gaseous hydrocarbon (0·75 mol.) was evolved and 2·5 mols. of ethylmagnesium bromide were consumed. An acid-soluble fraction consisting of reducing bases similar to those obtained from the primary nitro-olefin was isolated, and the neutral fraction was separated into an oil, $C_6H_{13}O_2N$ (26%), an oil, $C_8H_{17}ON$ (8%), and a large amount of non-volatile tar. The compound $C_6H_{13}O_2N$, which gave the nitrole reaction characteristic of a secondary nitro-group (Meyer, *loc. cit.*) and yielded a primary amine on reduction, was 2-*nitro*-3-*methylpentane*. The oil, $C_8H_{17}ON$, was colourless and contained one active hydrogen atom (Zerewitinoff); this excluded the possibility that it had the nitroso-structure (III; R = Et). It did not give the Meyer test for a nitro-paraffin, but on reduction it gave an amine, $C_8H_{19}N$. It must therefore be an oxime although, like the isomeric 3 : 3-dimethylhexan-4-one oxime, it failed to react with 2 : 4-dinitrophenylhydrazine or 2 : 4-dinitrophenylsemicarbazide.

On the basis of these results it is possible to build up a fairly complete picture of the course of the reaction of a Grignard reagent with a primary nitro-olefin, as shown in the scheme below for the reaction of ethylmagnesium bromide with 1-nitro-2-methylpropene. The initial step is addition (chiefly 1 : 4) of the Grignard reagent to the conjugated system to produce a complex (IV) which on hydrolysis gives the nitro-paraffin (I), but since (IV) contains the system C=N→O, addition of a second mol. of Grignard reagent occurs to give the complex (V) which on hydrolysis yields the oxime (II). The formation of reducing bases and of ethane can be explained only by the assumption that part of the nitro-olefin undergoes 1 : 2-addition of Grignard reagent to give a complex (VI) which reacts with more Grignard reagent to give dialkylhydroxylamines; this process is analogous to the formation of dialkylhydroxylamines by the action of Grignard reagents on nitro-paraffins (this series, Part IX; Bevad, *Ber.*, 1907, **40**, 3065). Unfortunately, the nitro-olefin reaction produces mixtures of bases of so complex a nature and in such small amount that it has not been possible to isolate pure products which would establish with certainty the occurrence of 1 : 2-addition.



The secondary nitro-olefin underwent a similar series of reactions. The formation of 2-nitro-3-methylpentane in the reaction of 2-nitrobut-2-ene with ethylmagnesium bromide is clear evidence of 1 : 4-addition, and the isolation of reducing bases and the formation of a hydrocarbon again point to the occurrence of some 1 : 2-addition. The nature of the reaction of the 1 : 4-addition complex of the secondary nitro-olefin with more Grignard reagent is obscure; if it followed the same course as for the primary nitro-olefins the product would be a nitroso-compound (III). However, as stated above, although a product of the same empirical

formula as (III) was isolated, it appeared to be an oxime, which may result from a rearrangement of (III) or of its complex (VII). Such a rearrangement might also explain the extensive tar formation, which was observed only in the case of the secondary nitro-olefin.



(VII.) (III.)

Experimental.

Microanalyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

Nitroethylene and Ethylmagnesium Bromide.—A solution of nitroethylene (Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) (11·2 g.) in dry ether (60 c.c.) was added during 1 hour to a stirred solution of ethylmagesium bromide (from 50 g. ethyl bromide) in ether (250 c.c.) at 10—15°, and the mixture was then stirred and refluxed for 2 hours; gas evolution had then ceased. This gas (2100 c.c. at N.T.P.) did not react with bromine and did not liquefy on cooling to − 80°. The mixture was cooled in ice, and water (100 c.c.) was added dropwise; a further 2300 c.c. of gas were evolved. The mixture was acidified to Congo-red with dilute sulphuric acid, separated, and the aqueous layer, made strongly alkaline with sodium hydroxide, was extracted with ether in a continuous extractor. The extract was dried (NaOH) and distilled, giving a strongly basic oil (4·8 g.) which boiled over a wide range under reduced pressure and reduced ammoniacal silver nitrate. Catalytic hydrogenation in the presence of Raney nickel gave a non-reducing basic oil which distilled over a wide range and from which no crystalline derivative could be prepared.

The ethereal solution containing the acid-insoluble products was dried and distilled. Two fractions were isolated: (1) b. p. 50—65°/30 mm., and (2) b. p. 90—100°/30 mm. Redistillation of fraction (1) gave 1-nitrobutane (3·2 g.) as a colourless oil, b. p. 150—152°, which gave a positive test for the presence of a primary nitro-group (Meyer, *loc. cit.*). A solution of the nitro-compound in dilute aqueous sodium hydroxide, run into excess of 20% sulphuric acid at 10—15°, gave *n*-butaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. with an authentic specimen, 126°).

Redistillation of fraction (2) gave hexan-3-one oxime (4·7 g.) as a colourless oil, b. p. 98—100°/30 mm. (Found: N, 12·0. Calc. for $C_6H_{13}ON$: N, 12·2%). The oxime, with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, gave hexan-3-one 2 : 4-dinitrophenylhydrazone as red needles, m. p. 128—129°; Allen (*loc. cit.*) gives m. p. 129° (Found: C, 50·95; H, 5·5; N, 20·4. Calc. for $C_{12}H_{16}O_4N_4$: C, 51·4; H, 5·7; N, 20·0%).

3-*Aminohexane.* A solution of hexan-3-one oxime (3·5 g.) in methyl alcohol (35 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was acidified with hydrochloric acid and evaporated to dryness, and the residue after being washed with acetone afforded 3-aminohexane hydrochloride, m. p. 225—226°. Bevad (*J. pr. Chem.*, 1901, **63**, 230) gives m. p. 227—229° (Found: Cl, 25·2. Calc. for $C_6H_{15}N,HCl$: Cl, 25·9%). The hydrochloride with potassium cyanate in boiling aqueous solution gave 3-*ureidohexane*, m. p. 150—151° (Found: C, 58·65; H, 11·3; N, 18·9. $C_7H_{16}ON_2$ requires C, 58·35; H, 11·1; N, 19·35%).

Nitroethylene and n-*Butylmagnesium Bromide.*—Nitroethylene (14·6 g.) was brought into reaction with a Grignard solution, prepared from *n*-butyl bromide (75·5 g.), as described above for ethylmagnesium bromide. When reaction was complete the mixture was cooled in ice, decomposed by cautious addition of aqueous acetic acid (150 c.c. of 20%), and separated. The ethereal solution was washed with dilute sodium hydrogen carbonate solution, dried, and distilled. This gave two fractions: (1) b. p. 84°/21 mm., and (2) b. p. 120—123°/12 mm. Fraction (1), a colourless, sweet-smelling oil which gave the nitrolic acid reaction, was 1-nitrohexane (Found: C, 55·15; H, 9·85; N, 10·65. Calc. for $C_6H_{13}O_2N$: C, 54·95; H, 9·9; N, 10·7%). Hydrolysis with concentrated hydrochloric acid at 150° in a sealed tube for 12 hours gave hexoic acid, which was characterised as the amide, m. p. 98°, and the anilide, m. p. 95°. Fraction (2) was a colourless oil, *decan-5-one oxime* (Found: C, 70·5; H, 12·45; N, 7·95. $C_{10}H_{21}ON$ requires C, 70·2; H, 12·3; N, 8·2%).

n-*Hexylamine.* A solution of 1-nitrohexane (5·5 g.) in methyl alcohol (80 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was acidified with hydrochloric acid and evaporated to dryness, giving the hydrochloride (2·25 g.) which, after being washed with acetone, had m. p. 217—218° (Found: Cl, 25·75. Calc. for $C_6H_{15}N,HCl$: Cl, 25·9%). With potassium cyanate in boiling aqueous solution the hydrochloride gave *n*-hexylurea, m. p. 108° (cf. Norstedt and Wahlforss, *Ber.*, 1892, **25**, ref. 637).

5-*Aminodecane.* 5-Decanone oxime (3 g.) was dissolved in methyl alcohol and hydrogenated over Raney nickel at 20°/1 atm. After filtration and evaporation, 5-aminodecane was obtained as an oil which on treatment with phenyl *iso*cyanate gave 5-*phenylureidodecane*, m. p. 129—130°, colourless needles from acetic acid (Found: C, 73·85; H, 10·1; N, 10·15. $C_{17}H_{28}ON_2$ requires C, 73·9; H, 10·15; N, 10·15%).

1-*Nitro*-2-*methylprop*-1-*ene and Ethylmagnesium Bromide.*—1-Nitro-2-methylprop-1-ene (25 g.; Levy and Scaife, in the press) was dissolved in dry ether (25 c.c.) and cooled to 0°. A solution of ethylmagnesium bromide (125 c.c.) was added during 1 hour with stirring at 0—5°; no gas was evolved. The temperature was raised to 15° and a further 475 c.c. of the Grignard solution were added during 1 hour at 15—25°; 5·5 l. of ethane were evolved. The mixture was refluxed for 12 hours, cooled and treated dropwise with water (125 c.c.) which liberated a further 5·5 l. of ethane. After acidification with dilute hydrochloric acid, the mixture was separated and the aqueous portion was made strongly alkaline with sodium hydroxide and steam-distilled. From the distillate was obtained by isolation with ether a small amount of a strongly basic oil which reduced ammoniacal silver nitrate.

The ethereal solution, containing the acid-insoluble products, was dried and distilled, giving two

fractions. Fraction (1) (6·2 g.), a colourless, sweet-smelling oil, b. p. 70°/25 mm., which gave the nitrolic acid reaction, was *1-nitro-2 : 2-dimethylbutane* (I; R = Et) (Found: C, 54·75; H, 9·8; N, 10·8. $C_6H_{13}O_2N$ requires C, 54·95; H, 9·9; N, 10·7%). Fraction (2) (10·1 g.), a colourless crystalline solid, b. p. 100°/25 mm., was *3 : 3-dimethylhexan-4-one oxime* (II; R = Et), m. p. 42—43°, from light petroleum (b. p. 40—60°) (Found: C, 67·55; H, 12·1; N, 9·65. $C_8H_{17}ON$ requires C, 67·15; H, 11·9; N, 9·8%).

1-Amino-2 : 2-dimethylbutane. A solution of the nitro-compound (4·3 g.) in methyl alcohol (50 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was fractionally distilled, giving the amine as a colourless oil (2·3 g.), b. p. 110—115° (Found: equiv., 99·9. Calc. for $C_6H_{15}N$: equiv. 101). The picramide, yellow needles from alcohol, had m. p. 89° (Found: C, 46·25; H, 5·25; N, 17·85. Calc. for $C_{12}H_{16}O_6N_4$: C, 46·15; H, 5·1; N, 18·0%). The benzenesulphonyl derivative had m. p. 59° (Found: N, 6·05. Calc. for $C_{12}H_{19}O_2NS$: N, 5·8%). Drake, Kline, and Rose (*J. Amer. Chem. Soc.*, 1934, **56**, 2079) give m. p. 88—88·5° for the picramide and m. p. 59—59·5° for the benzenesulphonyl derivative of 1-amino-2 : 2-dimethylbutane.

4-Amino-3 : 3-dimethylhexane. A solution of 3 : 3-dimethylhexan-4-one oxime (6·8 g.) in methyl alcohol (70 c.c.) was stirred in an autoclave with Raney nickel and hydrogen at 100°/100 atm. until absorption ceased. The filtered solution was acidified with hydrochloric acid and evaporated to dryness. The product was dissolved in a little water, washed with ether, basified with sodium hydroxide, extracted with ether, and the extract dried (KOH). Distillation gave *4-amino-3 : 3-dimethylhexane* (3·3 g.) as a colourless oil, b. p. 152° (Found: equiv., 130·7. $C_8H_{19}N$ requires equiv., 129). Reaction with phenyl *iso*cyanate in dry ether gave *4-phenylureido-3 : 3-dimethylhexane*, m. p. 157—158°, colourless needles from acetic acid (Found: C, 72·45; H, 9·65; N, 11·35. $C_{15}H_{24}ON_2$ requires C, 72·6; H, 9·7; N, 11·3%). With picryl chloride in alcohol the base gave *4-picrylamino-3 : 3-dimethylhexane*, m. p. 60°, orange plates from alcohol (Found: C, 49·6; H, 5·5; N, 16·65. $C_{14}H_{20}O_6N_4$ requires C, 49·4; H, 5·9; N, 16·45%).

2-Nitrobut-2-ene and Ethylmagnesium Bromide.—2-Nitrobut-2-ene (62 g.; this series, Part III) was brought into reaction, under the conditions described above for nitroethylene, with a Grignard solution prepared from ethyl bromide (218 g.); 10 l. of ethane were evolved. Distillation of the acid-insoluble portion of the product under reduced pressure left a large non-volatile tarry residue, and repeated fractionation separated the distillate into two fractions. The acid-soluble portion (12 g.), fraction (3), was isolated by treatment of the aqueous solution with sodium hydroxide, followed by extraction with ether in a continuous extractor. Fraction (1) (20·3 g.), a colourless oil, b. p. 68—70°/25 mm., which gave the *ψ*-nitrole reaction (Meyer, *loc. cit.*), was *2-nitro-3-methylpentane* (Found: C, 54·75; H, 9·6; N, 10·8. $C_6H_{13}O_2N$ requires C, 54·95; H, 9·9; N, 10·7%). Fraction (2) (7 g.) was a colourless oil, b. p. 98—100°/20 mm., which did not give the Meyer nitro-paraffin test and did not react with 2 : 4-dinitrophenylhydrazine in acid solution (Found: C, 67·8; H, 11·8; N, 10·1; active H (Zerewitinoff) 0·63. $C_8H_{17}ON$ requires C, 67·15; H, 11·9; N, 9·8; 1 active H, 0·7%). On reduction with Raney nickel and hydrogen in methyl alcohol at 100°/100 atm. fraction (2) gave a colourless basic oil, b. p. 157—158° (Found: equiv., 130·2. $C_8H_{19}N$ requires equiv., 129), which gave a hydrochloride of indefinite m. p., readily soluble in alcohol, acetone, and ether (Found: Cl, 21·65. $C_8H_{19}N$,HCl requires Cl, 21·45%).

Fraction (3) was a strongly basic oil, boiling over a wide range (40—110°/10 mm.); it reduced ammoniacal silver nitrate and absorbed hydrogen in the presence of a nickel catalyst, but no crystalline derivatives could be obtained from the resulting mixture of amines.

2-Amino-3-methylpentane. A solution of 2-nitro-3-methylpentane (10 g.) in methyl alcohol (100 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was distilled, giving *2-amino-3-methylpentane* as a colourless oil, b. p. 105—107° (Found: equiv., 102·7. $C_6H_{15}N$ requires equiv., 101). With picryl chloride it gave a *picramide*, m. p. 58—59° (Found: C, 46·3; H, 5·1; N, 17·7. $C_{12}H_{16}O_6N_4$ requires C, 46·15; H, 5·1; N, 18·0%).

The author wishes to acknowledge the interest and advice of Dr. H. A. Piggott and Mr. J. D. Rose in this work.

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290. *Aliphatic Nitro-compounds. Part XI. Preparation of Nitro-paraffins by 1 : 4-Addition of Organometallic Halides to α-Nitro-olefins.**

By GERARD D. BUCKLEY and ERIC ELLERY.

A series of hitherto unknown or inaccessible nitro-paraffins has been prepared by 1 : 4-addition of alkyl- or aryl-magnesium halides or alkylzinc halides to α-nitro-olefins. By carrying out the reaction below 10° and avoiding excess of organometallic halide secondary reactions are almost completely suppressed, but the yield of nitro-paraffin never exceeds 65% and is frequently less, apparently owing to the simultaneous occurrence of some 1 : 2-addition.

THE formation of nitro-paraffin derivatives in high yield by the action of Grignard reagents on di- and tri-phenylnitroethylenes has been described by Kohler and Stone (*J. Amer. Chem. Soc.*, 1930, **52**, 761). Under similar conditions simpler nitro-olefins yield a complex mixture of

* Cf. B.P. 571,804.

products of which the nitro-paraffin forms only a small proportion (Part X of this series). The nitro-paraffins are formed by 1 : 4-addition of the Grignard reagent to the conjugated system and the by-products arise partly from 1 : 2-addition and partly from the action of excess of Grignard reagent on the initial addition products.

The results described in Part X indicate that the initial addition occurs much more readily than the subsequent reactions, and it has now been found that, by working at low temperatures and avoiding excess of Grignard reagent, secondary reactions are suppressed, and nitro-paraffins are obtained as the main products. The reaction has been carried out on a variety of nitro-olefins and organomagnesium halides (and one alkylzinc halide) and appears to be quite general. The yields are frequently poor, but are probably capable of considerable improvement, since 60—65% yields were obtained consistently in the only two examples in which any attempt was made to determine the optimum conditions of reaction and isolation, *viz.*, the reaction of *n*-butylmagnesium bromide with nitroethylene and of ethylmagnesium bromide with 1-nitro-2-methylprop-1-ene.

In the two cases in which alkylmagnesium iodides were used small amounts of crystalline by-products were formed, but owing to the smallness of the amounts available they were not further investigated; no trace of these compounds was found when the corresponding bromides were used.

Experimental.

Microanalyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

1-*Nitro*-2 : 2-*dimethylbutane*.—(a) *From ethylmagnesium bromide*. A solution of ethylmagnesium bromide, prepared from ethyl bromide (48 g.) in ether (200 c.c.), was added during 1 hour to a stirred solution of 1-nitro-2-methylprop-1-ene (40 g.; Levy and Scaife, in the press) in pure, dry ether (400 c.c.), the temperature being held at 0—10°. The mixture was refluxed for 1 hour, cooled in ice, and treated cautiously with a solution of acetic acid (20 c.c.) in water (160 c.c.). The ethereal layer was washed with dilute sodium carbonate solution, dried, and distilled, giving 1-nitro-2 : 2-dimethylbutane (30·2 g.; 60% of theory) as a sweet-smelling oil, b. p. 168—170° (cf. Part X).

(b) *From ethylmagnesium iodide*. To an ice-cold, stirred solution of ethylmagnesium iodide, prepared in the usual manner from ethyl iodide (78 g.) in ether (200 c.c.), was added 1-nitro-2-methylprop-1-ene (34 g.) in ether (40 c.c.) during 1 hour at 0—10°. The mixture was stirred at 20° for 2 hours and worked up as before. Distillation of the crude product gave 25·3 g. (57·5% theory) of 1-nitro-2 : 2-dimethylbutane, b. p. 168—170°. The undistilled residue was crystallised from alcohol, giving colourless granules (0·4 g.) of an unidentified product, m. p. 182° (Found : C, 52·25; H, 7·55; N, 14·75. $C_8H_{14}O_3N_2$ requires C, 51·6; H, 7·5; N, 15·05%).

(c) *From ethylzinc iodide*. A solution of ethylzinc iodide in dry toluene, prepared from ethyl iodide (47 g.), was stirred at 0—10° and treated with a solution of 1-nitro-2-methylprop-1-ene (15 g.) in pure, dry ether (15 c.c.) during 1 hour. The mixture was then stirred at 50° for 3 hours, poured into ice, and treated with glacial acetic acid (20 c.c.). The organic layer was separated, dried, and fractionated to give 1-nitro-2 : 2-dimethylbutane (5·6 g.), b. p. 78—80°/30 mm.

Nitroneopentane.—A solution of methylmagnesium iodide, prepared from methyl iodide (71 g.), was brought into reaction with 1-nitro-2-methylprop-1-ene (34 g.) as described above for ethylmagnesium iodide. After working up in the usual manner, the crude product was distilled, giving *nitroneopentane* (16·2 g.; 42%) as a colourless oil, b. p. 77—78°/65 mm. (Found : C, 51·65; H, 9·35; N, 11·95. $C_5H_{11}O_2N$ requires C, 51·3; H, 9·4; N, 11·95%). The non-volatile residue crystallised on cooling and was purified by recrystallisation from alcohol and benzene, giving colourless prisms, m. p. 144° (Found : C, 46·8; H, 7·8; N, 13·05. $C_4H_9O_2N$ requires C, 47·05; H, 7·85; N, 13·7%).

1-*Nitro*-2 : 2 : 3 : 3-*tetramethylpentane*.—A solution of *tert.*-amylmagnesium chloride, prepared from *tert.*-amyl chloride (21·3 g.) by the method of Whitmore and Badertscher (*J. Amer. Chem. Soc.*, 1933, **55**, 1559), was brought into reaction with 1-nitro-2-methylprop-1-ene (10 g.) as described above for ethylmagnesium iodide. After isolation as before, the crude product was fractionated to give a colourless oil (6·5 g.), b. p. 102—105°/11 mm., having a camphor-like odour (Found : C, 62·55; H, 10·65; N, 8·45. $C_9H_{19}O_2N$ requires C, 62·45; H, 10·95; N, 8·1%).

aaββ-Tetramethylvaleric Acid.—1-Nitro-2 : 2 : 3 : 3-tetramethylpentane (6 g.) was mixed with concentrated aqueous hydrochloric acid (20 c.c.) and heated in a sealed tube at 150° for 6 hours. The product was diluted with water and extracted with ether, and the ethereal solution washed thoroughly with dilute aqueous sodium carbonate. The alkaline extract was acidified with dilute sulphuric acid, extracted with ether, and the dried ethereal solution was distilled, giving *aaββ-tetramethylvaleric acid*, b. p. 122°/15 mm., m. p. 89—90° [from light petroleum (b. p. 40—60°)] (Found : C, 68·8; H, 11·4; equiv., 158. $C_9H_{18}O_2$ requires C, 68·35; H, 11·4%; equiv., 158).

1-*Nitro*-2 : 2-*dimethylpent*-4-*ene*.—Allyl bromide (41 g.) in dry ether (250 c.c.) was converted into the Grignard reagent by the method of Gilman and McGlumphy (*Bull. Soc. chim.*, 1928, **43**, 1322), and the resulting solution filtered through glass wool and cooled to 0°. A solution of 1-nitro-2-methylprop-1-ene (20 g.) in dry ether (50 c.c.) was then added with stirring during 1 hour at 0—10°. After being stirred at 20° for 2 hours the mixture was poured into ice, treated with acetic acid (25 c.c.), and separated. The ethereal solution was dried and distilled under reduced pressure, giving much unchanged 1-nitro-2-methylprop-1-ene and a small yield (6·5 g.) of 1-*nitro*-2 : 2-*dimethylpent*-4-*ene*, b. p. 77°/20 mm. (Found : N, 9·7. $C_7H_{13}O_2N$ requires N, 9·8%). This was a pleasant-smelling oil, which gave the Meyer test for a primary nitro-compound, and reacted with bromine in carbon tetrachloride to give a liquid bromo-derivative.

1-*Nitrohexane*.—Nitroethylene (21 g.) dissolved in dry ether (100 c.c.) was added during 1 hour to a stirred solution of *n*-butylmagnesium bromide (0·4 g. mol.) in ether (250 c.c.). A vigorous exothermic reaction ensued, and the temperature was maintained below 0° with a freezing mixture; when the addition was complete the mixture was stirred for 1 hour at 20° and the complex decomposed by cautious addition of a solution of acetic acid (48 c.c.) in water (240 c.c.). After being stirred for a further 45 minutes, the mixture was steam-distilled, the ethereal layer of distillate separated, dried, and distilled, giving 38·6 g.(65%) of 1-nitrohexane, b. p. 84°/21 mm.; $n_D^{20°}$ 1·4270 (cf. Part X of this series) (Found : N, 10·65. Calc. for $C_6H_{13}O_2N$: N, 10·7%).

2-*Nitro*-3-*methylpentane*.—2-Nitrobut-2-ene (50 g.; this series, Part III) was dissolved in dry ether (250 c.c.) and brought into reaction with a solution of ethylmagnesium bromide (0·75 g. mol.) in ether (375 c.c.) as described above for the preparation of 1-nitrohexane. After working up in the usual way 2-nitro-3-methylpentane (27·7 g.; 42·5%) was obtained as a colourless oil, b. p. 70—73°/20 mm.; $n_D^{20°}$ 1·4320 (cf. Part X of this series) (Found : N, 10·8. Calc. for $C_6H_{13}O_2N$: N, 10·7%).

2-*Nitropentane*.—2-Nitroprop-1-ene (17·4 g.; this series, Part I) dissolved in dry ether (60 c.c.) was brought into reaction with ethylmagnesium bromide (from 22 g. of ethyl bromide) in ether (100 c.c.) as described above for the preparation of 1-nitrohexane. After working up in the usual way the crude distillate (b. p. 40—60°/12 mm.) was washed with aqueous sodium hydrogen sulphite to remove unchanged 2-nitroprop-1-ene, dried, and fractionated, giving a colourless oil, b. p. 148—150°. 2-*Nitropentane* is a pleasant-smelling oil, soluble in dilute aqueous sodium hydroxide, which gives the Meyer test for a secondary nitro-compound (Found : C, 51·65; H, 9·7; N, 11·8. $C_5H_{11}O_2N$ requires C, 51·3; H, 9·4; N, 11·95%). Reduction of 2-nitropentane (3·5 g.) in methyl alcohol with hydrogen in the presence of Raney nickel in the usual way gave 2-aminopentane, isolated as the hydrochloride (3·4 g.). Reaction of the base with phenyl *iso*cyanate gave the phenylurea, m. p. 119—120°, colourless plates from aqueous alcohol. Mailhe (*Bull. Soc. chim.*, 1905, **33**, 966) gives m. p. 120° for *N*-phenyl-*N'*-α-methylbutylurea (Found : N, 13·6. Calc. for $C_{12}H_{18}ON_2$: N, 13·6%).

2-*Nitro*-3-*methylpentadecane*.—A solution of dodecylmagnesium bromide (from 55 g. of dodecyl bromide) in dry ether (250 c.c.) was added during 1 hour to a stirred solution of 2-nitrobut-2-ene (30 g.) in dry ether (150 c.c.) at 0—5°. The mixture was refluxed for 1 hour, cooled, and treated cautiously with aqueous acetic acid (120 c.c. of 20%). The mixture was stirred until all the magnesium salts had dissolved, and the ethereal layer was dried, concentrated, and the residue repeatedly fractionated in a vacuum to give the nitro-compound (20 g.) as a pale yellow oil, b. p. 111—115°/0·06 mm. (Found : C, 71·0; H, 12·1; N, 5·85. $C_{16}H_{33}O_2N$ requires C, 70·85; H, 12·2; N, 5·2%). This gave the Meyer test for a secondary nitro-compound and formed a crystalline sodium salt on treatment with alcoholic sodium hydroxide.

2-*Amino*-3-*methylpentadecane*.—The nitro-compound (10 g.) was catalytically reduced in methyl alcohol in the presence of Raney nickel at ordinary temperature and pressure. Distillation of the filtered solution gave the *amine* (5·5 g.) as a colourless oil, b. p. 158—160°/11 mm. (Found : equiv., 237. $C_{16}H_{35}N$ requires equiv., 241). An aqueous solution of the hydrochloride, on being boiled with excess potassium cyanate, deposited colourless crystals of 2-*ureido*-3-*methylpentadecane*, m. p. 122—123° (from alcohol) (Found : C, 71·4; H, 12·4; N, 9·9. $C_{17}H_{36}ON_2$ requires C, 71·8; H, 12·7; N, 9·9%).

2-*Nitro*isopropylcyclo*hexane*.—*cyclo*Hexylmagnesium bromide (from 81·5 g. of *cyclo*hexyl bromide) was brought into reaction with 1-nitroprop-1-ene (29 g.; this series, Part I) as described above for the preparation of 1-nitrohexane. After decomposition of the complex the ethereal layer was concentrated and the residue dissolved in alcohol (200 c.c.), treated with aqueous sodium hydroxide (35 c.c. of 32%) at 0—5°, the solution diluted with water (400 c.c.), and washed with ether. The aqueous solution was made acid to Congo-red with concentrated hydrochloric acid at 0—5° and extracted with ether. The extract was dried and distilled, giving 2-*nitro*isopropylcyclo*hexane* as a pale yellow oil, b. p. 122°/16 mm. (Found : C, 63·4; H, 9·7; N, 8·2. $C_9H_{17}O_2N$ requires C, 63·15; H, 9·95; N, 8·2%).

2-*Nitro*-3-*phenylbutane*.—Phenylmagnesium bromide (from 51 g. of bromobenzene) was brought into reaction with 2-nitrobut-2-ene (20 g.) as described above for the preparation of 1-nitrohexane. After isolation in the usual manner the product was distilled under reduced pressure, giving impure 2-nitro-3-phenylbutane (22·5 g.), b. p. 118—120°/13 mm. This material, which appeared to contain some diphenyl, was not further purified but was reduced with hydrogen in methyl alcohol in the presence of Raney nickel at ordinary temperature and pressure. The filtered solution was acidified with hydrochloric acid and evaporated to dryness on the steam-bath, the residue dissolved in water, and washed with ether. The aqueous solution was then basified with concentrated sodium hydroxide and extracted with ether. The extract was dried (KOH) and distilled, giving the *amine* as a colourless oil (10·7 g.), b. p. 87°/12 mm. (Found : equiv., 147. $C_{10}H_{15}N$ requires equiv., 149). Reaction with picryl chloride gave 2-*picrylamino*-3-*phenylbutane*, m. p. 119—120°, yellow plates from alcohol (Found : N, 15·65. $C_{16}H_{16}O_6N_4$ requires N, 15·55%).

2-*Nitro*-3-*phenylheptane*.—2-Nitro-1-phenylprop-1-ene (32 g.; Alles, *J. Amer. Chem. Soc.*, 1932, **54**, 272) dissolved in dioxan (120 c.c.) was added during 1 hour to a stirred ethereal solution (150 c.c.) of butylmagnesium bromide (prepared from 42 g. of butyl bromide) at 0—5°. The mixture was stirred at 20° for 1 hour and the product isolated in the usual way. Distillation gave impure 2-nitro-3-phenylheptane (29 g.), b. p. 62—90°/0·02 mm., which was not further purified, but was reduced with hydrogen and Raney nickel in methyl alcohol. The filtered solution was acidified with hydrochloric acid and evaporated to dryness on the steam-bath; the residue was dissolved in water and washed with ether. The aqueous solution was basified with sodium hydroxide and the amine isolated with ether. Distillation gave 2-*amino*-3-*phenylheptane* as a colourless oil, b. p. 114—115°/9 mm. (Found : equiv., 191. $C_{13}H_{21}N$ requires equiv., 191). This material, apparently a mixture of stereoisomerides, gave a *hydrochloride* of indefinite m. p. (Found : Cl, 15·5. $C_{13}H_{21}N,HCl$ requires Cl, 15·6%). Attempts to prepare crystalline derivatives with benzoyl chloride, phenyl *iso*cyanate, picryl chloride, and nitrourea failed.

1-*Nitro*-2-(2-*furyl*)*hexane*.—A solution of 1-nitro-2-(2-furyl)ethylene (14 g.; Thiele and Landers, *Annalen*, 1909, **369**, 303) in dioxan (70 c.c.) was added during 1 hour at 0—10° to a stirred solution (150 c.c.) of *n*-butylmagnesium bromide prepared from *n*-butyl bromide (34·5 g.). The solution was stirred

at 20° for 18 hours, poured on ice, and the product isolated in the usual way, giving 1-*nitro*-2-(2-*furyl*)-*hexane* as a pale yellow oil (6·5 g.), b. p. 78—82°/0·4 mm. (Found: N, 7·2. $C_{10}H_{15}O_3N$ requires N, 7·1%).

1-*Nitro*-2-*benzylcyclohexane*.—An ethereal solution of benzylmagnesium chloride (prepared from 34 g. of benzyl chloride) was brought into reaction with 1-nitro*cyclo*hexene (32 g.; Wieland *et al.*, *Annalen*, 1921, **424**, 71) as described above for the preparation of 1-nitrohexane. Distillation of the product gave impure 1-nitro-2-benzyl*cyclo*hexane (23·5 g.), b. p. 91—115°/0·04 mm. This material, apparently containing 1 : 2-diphenylethane, was hydrogenated in the usual way over Raney nickel without further purification. The resulting amine was purified through its hydrochloride and finally distilled, giving a colourless oil (12·5 g.), b. p. 138—140°/11 mm. (Found: equiv., 191. Calc. for $C_{13}H_{19}N$: equiv., 189). This base, apparently a mixture of isomerides, was dissolved in benzene (50 c.c.) and shaken with 2N-hydrochloric acid (70 c.c.). After 45 minutes, the precipitated hydrochloride was collected; this appeared to be still a mixture, and no pure derivatives could be isolated from it. On standing overnight the mother liquor deposited a second precipitate which was collected and crystallised repeatedly from 2N-hydrochloric acid to give pure *cis*-2-benzyl*cyclo*hexylamine hydrochloride, m. p. 224°. This formed an acetyl derivative, m. p. 116°, and a benzoyl derivative, m. p. 155° (Found: C, 82·5; H, 8·25; N, 4·7. Calc. for $C_{20}H_{23}ON$: C, 81·9; H, 7·85; N, 4·8%). No m. p. depression was observed on admixture of these derivatives with authentic specimens prepared according to Schöpf and Boettcher (*Annalen*, 1926, **448**, 1).

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291. *Aliphatic Nitro-compounds. Part XII. Preparation and Reduction of 2-Nitroalkyl Cyanides.**

By G. D. Buckley, R. L. Heath, and J. D. Rose.

Interaction of alkali-metal cyanides (or mixtures of these with hydrogen cyanide) and α-nitro-olefins yields 2-nitroalkyl cyanides. 2-*Nitro*-1-*methyl*iso*propyl cyanide*, formed in 90% yield from 1-nitro-2-methylprop-1-ene and hydrogen cyanide–potassium cyanide, yields on catalytic reduction only minor quantities of the expected 2-*amino*-1-*methyl*iso*propyl cyanide* and 1 : 3-diamino-2 : 2-dimethylpropane, the major products being 2-*amino*-1-*methyl*iso*butyramide* and 5 : 5-*dimethyl*-2-(1-*carbamyl*iso*propyl*)*hexahydropyrimidine* (III). 2-*Nitropropyl cyanide*, 2-*nitro*iso*propyl cyanide*, and 2-*nitro*-1-*methylpropyl cyanide* on reduction yield, in addition to the amino-cyanides, some of the corresponding amino-amides.

In connection with a general programme of work on the addition reactions of the α-nitro-olefins, a study of the formation of 2-nitroalkyl cyanides by interaction of metallic cyanides (or mixtures of these with hydrogen cyanide) with α-nitro-olefins was undertaken. The reduction of the nitroalkyl cyanides was investigated as a potential technical route to certain 1 : 3-diamines and β-amino-acids required for synthetic work in another connection.

The literature contains only one reference to the interaction of a metal cyanide with an α-nitro-olefin. Hollemann (*Rec. Trav. chim.*, 1904, **23**, 283) showed that by interaction of β-nitrostyrene and potassium cyanide, two stereoisomerides of 1 : 4-dinitro-2-cyano-2 : 3-diphenylbutane (II) were formed.

$$Ph\cdot CH{:}CH\cdot NO_2 + HCN \longrightarrow \underset{\text{(I.)}}{Ph\cdot CH(CN)\cdot CH_2\cdot NO_2} \xrightarrow{Ph\cdot CH{:}CH\cdot NO_2} \underset{\text{(II.)}}{Ph\cdot C(CN)(CH_2\cdot NO_2)\cdot CHPh\cdot CH_2\cdot NO_2}$$

The primary reaction in the formation of (II) must be the addition of hydrogen cyanide to the nitro-olefin, giving 2-nitro-1-phenylethyl cyanide (I), which by further reaction with nitrostyrene affords (II).

Interaction of 1- and 2-nitroprop-1-ene with aqueous potassium cyanide gave 2-*nitro*iso*propyl cyanide* and 2-*nitro*-n-*propyl cyanide*, respectively, but the yields were poor (10—15%), much of the olefin being lost by polymerisation in the alkaline reaction medium. 2-Nitrobut-2-ene, which polymerises much less readily than its lower homologues, gave a 50% yield of 2-*nitro*-1-*methyl*-n-*propyl cyanide*, and 75—90% yields of *nitro*-tert.-*butyl cyanide* were obtained from 1-nitro-2-methylprop-1-ene and potassium cyanide, or mixtures of potassium cyanide with hydrogen cyanide. It was shown that hydrogen cyanide alone will not add to the ethylenic linkage of this nitro-olefin, but in the presence of small quantities of potassium cyanide (5—20% of the total of CN ion) excellent yields are obtained.

Surprising results were obtained in the reduction of the 2-nitroalkyl cyanides. Catalytic

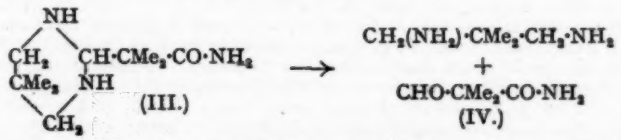
* Patent application pending.

reduction of 2-nitro*iso*propyl cyanide in methyl alcohol at ordinary temperature and pressure in presence of Raney nickel catalyst gave a low yield of *β-aminoisobutyramide*. Similar reduction of 2-nitro-1-methyl-*n*-propyl cyanide afforded a mixture of the expected aminoalkyl *cyanide* and *β-amino-α-methylbutyramide*, whilst reduction in the presence of anhydrous ammonia under pressure gave the amino-amide and some 1 : 3-diamino-2-methylpropane. In none of the above cases was the yield of reduction products good, and attention was turned for closer study to the more readily available nitro-*tert.*-butyl cyanide. Chemical reduction of this with iron and hydrochloric acid gave a 65% yield of *amino*-tert.-*butyl cyanide* and 5% of *β-amino-αα-dimethylpropionamide*. Catalytic reduction at ordinary temperature and pressure of the nitroalkyl cyanide in methyl alcohol with a 5% palladium on calcium carbonate catalyst gave the amino-amide in 90% yield and in methyl alcoholic ammonia at 100°/100 atms. with Raney nickel, 20% of the amino-amide and 15% of 1 : 3-diamino-2 : 2-dimethylpropane were obtained. On reduction in methyl alcohol with hydrogen at ordinary temperature and pressure in the presence of Raney nickel, four products were obtained : (*a*) the aminoalkyl cyanide (1·5%), (*b*) the diamine (1·5%), (*c*) the amino-amide (50%), and (*d*) a solid, $C_{10}H_{21}ON_3$ (20%), which separated as pearly plates, m. p. 150°, when the filtered reduction solution was concentrated.

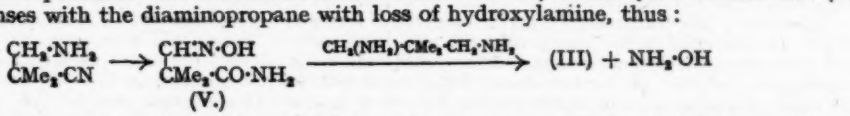
In attempting to prepare derivatives of the solid (*d*), it was observed that by the action of reagents for amines, the derivatives (*hydrochloride*, *picrate*, *benzoyl* derivative) which were obtained were identical with those formed directly from 1 : 3-diamino-2 : 2-dimethylpropane. It was, therefore, clear that the solid was a derivative of this diamine which was easily hydrolysed by acid and alkaline reagents, thus :

$$C_{10}H_{21}ON_3 + H_2O \longrightarrow CH_2(NH_2)\cdot CMe_2\cdot CH_2\cdot NH_2 + C_5H_9O_2N$$

By addition of a 2N-hydrochloric acid solution of 2 : 4-dinitrophenylhydrazine to the base, $C_{10}H_{21}ON_3$, in dilute hydrochloric acid, a 2 : 4-*dinitrophenylhydrazone*, $C_{11}H_{13}O_5N_5$, was obtained (*i.e.*, the derivative of a ketone or aldehyde, $C_5H_9O_2N$). This is formulated as α-carbamyl*iso*butaldehyde (IV), and the substance, $C_{10}H_{21}ON_3$, as 5 : 5-*dimethyl*-2-(1-*carbamylisopropyl*)-*hexahydropyrimidine* (III); the ease of fission of substituted hexahydropyrimidines is well recognised (cf. Veer, *Rec. Trav. chim.*, 1938, **57**, 989).



The mechanism of formation of the hexahydropyrimidine is obscure; Veer (*loc. cit.*) showed that derivatives of 1 : 3-diaminopropane condense with aldehydes merely on warming in alcoholic solution, but it is difficult to visualise conditions during a catalytic reduction which would convert the primary nitro-group, $-CH_2\cdot NO_2$, into the aldehyde group, –CHO. It is considered more probable that the intermediate in this case is β-carbamyl*iso*butaldoxime (V), which condenses with the diaminopropane with loss of hydroxylamine, thus :



The formation of amino-amides by mild catalytic reduction of the 2-nitroalkyl cyanides is surprising. It is thought that this is not simple addition of water to the aminoalkyl cyanide; an experiment was carried out in which nitro-*tert.*-butyl cyanide was shaken at room temperature in methyl alcohol with water (2 mols.) and Raney nickel (*i.e.*, the conditions of the hydrogenation). The aminoalkyl cyanide was recovered unchanged. It is possible that amide formation proceeds through an *iso*oxazole as intermediate product (*iso*oxazoles are known to undergo fission on hydrogenation), but no experimental proof for this can be given.

Experimental.

Analyses are by Mr. E. S. Morton. M. ps. are uncorrected.

2-Nitroisopropyl Cyanide.—1-Nitroprop-1-ene (50 g.; this series, Part I) in alcohol (240 c.c.) was added dropwise to a well-stirred solution of potassium cyanide (40 g.) in water (300 c.c.) at — 5° to 0°. The solution was stirred at 0° for a further 4 hours, acidified at 0—5° with 5N-hydrochloric acid (130 c.c.), concentrated under reduced pressure at 40° to 300 c.c., and after isolation with ether the *cyanide* (16·4 g.; 25%), b. p. 68—70°/0·5 mm., was obtained (Found : C, 42·6; H, 5·2; N, 23·9. $C_4H_6O_2N_2$ requires C, 42·1; H, 5·3; N, 24·5%).

β-Aminoisobutyramide.—The cyanide (3·25 g.) in methyl alcohol (50 c.c.) was shaken in hydrogen

at 25°/760 mm. in the presence of Raney nickel. Absorption (1916 c.c. of hydrogen) was complete in 3½ hours. The catalyst was separated, the alcohol removed, and the product distilled, giving the amide (0·44 g.; 15%), b. p. 75—82°/0·3 mm., which was identified as the *picrate*, m. p. 232° (Found: N, 20·6. $C_4H_{10}ON_2,C_6H_3O_7N_3$ requires N, 21·1%).

2-*Nitro*-n-*propyl Cyanide*.—This *compound* was prepared from 2-nitroprop-1-ene (50 g.; this series, Part I) and sodium cyanide (28·2 g.) as described for the *iso*-derivative above; it was obtained as a straw-coloured liquid (10 g.; 15%), b. p. 81—82°/0·5 mm. (Found: C, 42·7; H, 5·0. $C_4H_6O_2N_2$ requires C, 42·1; H, 5·3%).

2-*Nitro*-1-*methyl*-n-*propyl Cyanide*.—This *compound* was prepared from 2-nitrobut-2-ene (58 g.; this series, Part III) in alcohol (500 c.c.) and potassium cyanide (38 g.) in water (300 c.c.) at 10—20°. Isolation in the usual way yielded the cyanide (32 g.; 50%) as a pale yellow, mobile oil, b. p. 61—65°/0·2 mm. (Found: C, 47·0; H, 6·4. $C_5H_8O_2N_2$ requires C, 46·9; H, 6·2%).

Reduction of 2-*Nitro*-1-*methyl*-n-*propyl Cyanide*.—(a) *With Raney nickel at ordinary pressure.* The cyanide (10·4 g.) in methyl alcohol (80 c.c.) was shaken in hydrogen at 20°/750 mm. in the presence of Raney nickel. Absorption was 4930 c.c. of hydrogen at 0°/760 mm. [Calc. (3 mols.), 5460 c.c.]. The catalyst was separated and the product distilled, giving: (i) 2-Amino-1-methyl-*n*-propyl cyanide, b. p. 30°/0·05 mm. (0·5 g.), characterised as its *hydrochloride*, white crystals from alcohol–ether, m. p. 156° (Found: C, 44·6; H, 8·3; N, 20·8. $C_5H_{10}N_2$,HCl requires C, 44·6; H, 8·3; N, 20·8%). (ii) β-Amino-α-methylbutyramide, b. p. 145—155°/15 mm., 95—100°/0·05 mm. (1·7 g.), which solidified on keeping and after crystallisation from dry benzene had m. p. 62—63°. The amide was extremely deliquescent and satisfactory analyses could not be obtained. Neither the hydrochloride nor the picrate could be obtained in a crystalline condition, and the amide was characterised as the *picrolonate*, m. p. 214° (Found: N, 22·1. $C_5H_{12}ON_2,C_{10}H_8O_5N_4$ requires N, 22·1%).

(b) *With Raney nickel and anhydrous ammonia under pressure.* The cyanide (23 g.) in methyl alcohol (250 c.c.) and anhydrous ammonia (70 g.) was heated at 100° with hydrogen (initial pressure, 100 atms.) in an internally agitated stainless steel autoclave for 1 hour. The filtered solution was made acid to Congo-red with hydrochloric acid and evaporated to dryness at 40° under reduced pressure. The residue was treated with excess of aqueous potassium hydroxide and the product isolated with ether, giving: (i) 1 : 3-diamino-2-methylpropane, b. p. 60—70°/15 mm. (2 g.) (Found: equiv., 50. Calc.: 51); and (ii) β-amino-α-methylbutyramide, b. p. 145—155°/15 mm., m. p. 62—63°.

Nitro-tert.-*butyl Cyanide*.—(a) *From* 1-*nitro*-2-*methylprop*-1-*ene and potassium cyanide.* 1-Nitro-2-methylprop-1-ene (101 g.; Levy and Scaife, in the press) in alcohol (500 c.c.) was added slowly to a stirred aqueous solution of potassium cyanide (65 g. in 500 c.c.) at 20—25°. Stirring was continued for 6 hours and the mixture then acidified with 5N-hydrochloric acid (240 c.c.) at 5—10°. The white, crystalline precipitate was collected, washed with cold water and recrystallised from ether, giving *nitro*-tert.-*butyl cyanide* (96 g.; 75%), m. p. 42°, b. p. 66—67°/0·2 mm. (Found: C, 47·1; H, 6·1; N, 21·3. $C_5H_8O_2N_2$ requires C, 46·9; H, 6·2; N, 21·9%).

(b) *From* 1-*nitro*-2-*methylprop*-1-*ene, hydrogen cyanide, and potassium cyanide.* A mixture of the nitro-olefin (10·1 g.), hydrogen cyanide (6 g.), and potassium cyanide (0·325 g.; 5%) in 50% aqueous alcohol (50 c.c.) was stirred at room temperature for 24 hours. Water (50 c.c.) was then added and the solution at 0—5° made acid to Congo-red with hydrochloric acid. The precipitated cyanide was isolated with ether and recrystallised from ether, m. p. 42°. Yield, 10·3 g. (83%). In this preparation, the use of 1% of potassium cyanide reduced the yield to 10%; with 20% of potassium cyanide the yield was 87%; in the absence of potassium cyanide (hydrogen cyanide alone) no nitroalkyl cyanide was obtained.

(c) *From nitro*-tert.-*butyl acetate and potassium cyanide.* Nitro-*tert.*-butyl acetate (8 g.; this series, Part XVIII) was added dropwise to a vigorously stirred aqueous solution of potassium cyanide (4 g. in 25 c.c.) at 25—30°. Stirring was continued for 16 hours at 30°, the solution acidified at 0—5° with 5N-hydrochloric acid, and the precipitated cyanide crystallised from ether, m. p. 42°. Yield, 2·5 g. (40%).

Reduction of Nitro-tert.-*butyl Cyanide*.—(a) *With iron and hydrochloric acid.* A mixture of iron filings (35 g.), concentrated hydrochloric acid (10 c.c.), and water (75 c.c.) was allowed to react at 60—70° until evolution of hydrogen ceased. The cyanide (21 g.) in alcohol (50 c.c.) was then added at a rate sufficient to maintain the temperature of the vigorously stirred mixture at 60—70°, and stirring was continued at the same temperature for a further 8 hours. The mixture was filtered, acidified with concentrated hydrochloric acid, and evaporated to dryness, and the free bases, liberated by addition of an excess of 50% aqueous potassium hydroxide, were isolated with ether. Distillation gave: (i) *Amino*-tert.-*butyl cyanide* (10·2 g.; 65%), b. p. 63°/15 mm., m. p. 10° (Found: C, 61·5; H, 9·7. $C_5H_{10}N_2$ requires C, 61·2; H, 10·2%); *hydrochloride*, from alcohol, m. p. 260° (Found: C, 44·5; H, 8·2; N, 20·6. $C_5H_{10}N_2$,HCl requires C, 44·6; H, 8·2; N, 20·8%); *picrate*, from water, m. p. 183° (Found: C, 40·3; H, 3·8; N, 21·4. $C_5H_{10}N_2,C_6H_3O_7N_3$ requires C, 40·4; H, 3·9; N, 21·4%); *benzoyl* derivative, from alcohol, m. p. 122° (Found: C, 71·3; H, 6·6; N, 13·9. $C_{12}H_{14}ON_2$ requires C, 71·3; H, 6·9; N, 13·9%). Reduction of this aminoalkyl cyanide by shaking in methyl-alcoholic solution with hydrogen and Raney nickel at ordinary temperature and pressure afforded 1 : 3-*diamino*-2 : 2-*dimethylpropane*, b. p. 65°/15 mm., 153°/760 mm. (Found: C, 58·4; H, 13·6; N, 27·0. $C_5H_{14}N_2$ requires C, 58·8; H, 13·7; N, 27·4%); dihydrochloride, m. p. 259° [Komppa and Seron (*Ann. Acad. Sci. Fennicæ*, 1933, **37***A*, No. 7, 8; cf. *Chem. Abs.*, 1933, 3964) give m. p. 280—281°] (Found: C, 34·5; H, 8·6; N, 15·7; Cl, 40·1. Calc. for $C_5H_{14}N_2,2HCl$: C, 34·3; H, 9·1; N, 16·0; Cl, 40·6%); dipicrate, m. p. 234° (Komppa and Seron, *loc. cit.*, give m. p. 240°) (Found: C, 36·6; H, 3·6; N, 19·8. Calc. for $C_5H_{14}N_2,2C_6H_3O_7N_3$: C, 36·4; H, 3·6; N, 20·0%); *dibenzoyl* derivative, long needles from aqueous alcohol, m. p. 152° (Found: C, 73·7; H, 7·3; N, 9·0. $C_{19}H_{22}O_2N_2$ requires C, 73·5; H, 7·1; N, 9·0%). (ii) β-Amino-αα-dimethylpropionamide (1 g.; 5%), b. p. 145°/15 mm., which solidified and after crystallisation from dry benzene had m. p. 74—75° (Found: equiv. by titration, 115. Calc.: 116). This compound was highly deliquescent and satisfactory analyses could not be obtained; it was characterised as the following derivatives: *hydrochloride*, fine needles from absolute alcohol, m. p. 172° (Found: C, 39·6; H, 8·7;

N, 17·8; Cl, 23·3. $C_5H_{12}ON_2$,HCl requires C, 39·5; H, 8·5; N, 18·3; Cl, 23·3%); *hydrobromide*, plates from absolute alcohol, m. p. 202° (Found: C, 30·5; H, 6·2; N, 14·1; Br, 40·8. $C_5H_{12}ON_2$,HBr requires C, 30·5; H, 6·6; N, 14·2; Br, 40·6%); *picrate*, flat prisms from alcohol, m. p. 190° (Found: C, 38·4; H, 4·2; N, 20·4. $C_5H_{12}ON_2,C_6H_3O_7N_3$ requires C, 38·3; H, 4·3; N, 20·3%); *phenylurea*, prisms from alcohol, m. p. 199—200° (Found: C, 61·2; H, 7·0; N, 17·2. $C_{12}H_{17}O_2N_3$ requires C, 61·2; H, 7·2; N, 17·8%). The *benzoyl* derivative, prisms from alcohol–ether, m. p. 151° (Found: C, 65·5; H, 7·2; N, 12·5. $C_{12}H_{16}O_2N_2$ requires C, 65·4; H, 7·3; N, 12·7%), on being heated with excess of thionyl chloride, gave 2-benzamido-1 : 1-dimethyl-*tert.*-butyl cyanide, m. p. 122°, identical with that described above.

(b) *Reduction with hydrogen and Raney nickel at ordinary pressure.* The nitroalkyl cyanide (42 g.) in methyl alcohol (450 c.c.) was shaken in hydrogen in presence of Raney nickel at ordinary pressure and temperature. Absorption was 22·7 l. of hydrogen at N.T.P. [Calc. (3 mols.), 22·4 l.]. The catalyst was separated and the filtrate concentrated, giving a solid (*A*) and a liquid, separated by filtration. The liquid was distilled, giving the following: (i) Amino-*tert.*-butyl cyanide (0·5 g.; 1·5%), m. p. 10°. (ii) 1 : 3-Diamino-2 : 2-dimethylpropane (0·5 g.; 1·5%); dihydrochloride, m. p. 259°; dipicrate, m. p. 234°. (iii) β-Amino-αα-dimethylpropionamide (19 g.; 50%), m. p. 74—75°. The solid (*A*), above, recrystallised from absolute alcohol, gave 5 : 5-*dimethyl*-2-(1-*carbamylisopropyl*)*hexahydropyrimidine* (6·5 g.; 20%) in pearly plates, m. p. 150° (Found: C, 60·2; H, 10·1; N, 20·6. $C_{10}H_{21}ON_3$ requires C, 60·3; H, 10·5; N, 21·0%). On addition of a dry, ethereal solution of hydrogen chloride to the base in alcohol at 0—10°, 1 : 3-diamino-2 : 2-dimethylpropane dihydrochloride, m. p. and mixed m. p. with an authentic specimen 259°, separated in 42% yield. Similarly, addition of hot, aqueous picric acid to an alcoholic solution of the hydropyrimidine gave 1 : 3-diamino-2 : 2-dimethylpropane dipicrate, m. p. and mixed m. p. 234°, and benzoylation by the Schotten–Baumann procedure gave 1 : 3-dibenzamido-2 : 2-dimethylpropane, m. p. and mixed m. p. 152°. Addition of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid to a solution of the pyrimidine in hydrochloric acid gave a pale yellow, crystalline precipitate, which, crystallised from methyl alcohol, yielded *β-carbamylisobutaldehyde* 2 : 4-*dinitrophenylhydrazone*, m. p. 196° (Found: C, 44·7; H, 4·4; N, 23·6. $C_{11}H_{13}O_5N_5$ requires C, 44·7; H, 4·4; N, 23·7%).

(c) *Reduction with hydrogen and palladium.* The nitro-cyanide (10 g.) in methyl alcohol (50 c.c.) was shaken in hydrogen with a 5% palladium on calcium carbonate catalyst at ordinary pressure. Absorption was 5·2 l. of hydrogen at N.T.P. [Calc. (3 mols.), 5·25 l.]. The catalyst was removed and the solution distilled, yielding β-amino-αα-dimethylpropionamide, m. p. 74—75° (8·0 g.; 89%).

(d) *Reduction with hydrogen and Raney nickel in presence of anhydrous ammonia.* The nitro-cyanide (45 g.) in methyl alcohol (250 c.c.) and anhydrous ammonia (140 g.) was heated at 100° in an internally agitated, stainless steel autoclave with hydrogen at 100 atms. initial pressure and Raney nickel (10 g.). Hydrogenation was complete in 1 hour. After evaporation of the ammonia, the catalyst was removed and the product distilled, giving: (i) 1 : 3-Diamino-2 : 2-dimethylpropane, b. p. 65°/15 mm. (5·5 g.; 15%). (ii) β-Amino-αα-dimethylpropionamide, m. p. 74—76° (8·2 g.; 20%).

β-Amino-αα-dimethylpropionic Acid.—β-Amino-αα-dimethylpropionamide (9·2 g.) was refluxed for 4 hours with 40% sulphuric acid (90 c.c.). The solution was diluted with water (300 c.c.) and barium carbonate (slight excess calculated on the sulphuric acid) was added slowly to the boiling solution through which a current of steam was passed to remove the ammonia. The excess of barium carbonate was decomposed by neutralisation (to Congo-red) with 2N-sulphuric acid, and the barium sulphate removed by filtration. The filtrate was concentrated to 75 c.c., and traces of sulphuric acid were precipitated with lead carbonate, the lead sulphate was filtered off, and the filtrate saturated with hydrogen sulphide. After removal of lead sulphide, the filtrate was concentrated and yielded β-amino-αα-dimethylpropionic acid, which separated from aqueous alcohol as large hexagonal prisms, m. p. 246° (decomp.) in 82% yield (Kohn and Schmidt, *Monatsh.*, 1907, **28**, 1055, give decomp. *ca.* 220°) (Found: C, 51·1; H, 9·4; N, 12·3. Calc. for $C_5H_{11}O_2N$: C, 51·3; H, 9·4; N, 12·0%).

Methyl β-Amino-αα-dimethylpropionate.—The acid was esterified in methyl alcohol with dry hydrogen chloride in the usual way; evaporation of the methyl alcohol yielded the *methyl ester hydrochloride*, m. p. 164° (80% yield) (Found: C, 43·0; H, 8·2; N, 8·2. $C_6H_{13}O_2N$,HCl requires C, 43·0; H, 8·4; N, 8·4%). Addition of 10N-sodium hydroxide to an aqueous solution of the hydrochloride, followed by isolation with ether and distillation, afforded the *methyl* ester, b. p. 57°/11 mm., which separated from dry ether as highly deliquescent prisms, m. p. 64° (Found: C, 54·8; H, 9·9; N, 10·5. $C_6H_{13}O_2N$ requires C, 55·0; H, 9·9; N, 10·7%). The ester was completely unchanged after standing for 2 days at 0° with methyl alcoholic ammonia; with concentrated aqueous ammonia, at 60° for 3 days, hydrolysis to the acid occurred. The *ethyl ester hydrochloride*, similarly formed, had m. p. 91° (Found: C, 45·6; H, 8·4; N, 7·8; Cl, 19·7. $C_7H_{15}O_2N$,HCl requires C, 46·2; H, 8·8; N, 7·7; Cl, 19·7%).

β-Benzamido-αα-dimethylpropionic acid, m. p. 151° (Kohn and Schmidt, *loc. cit.*, give m. p. 149—151°) (3 g.) was treated with freshly distilled thionyl chloride (6·5 c.c.; 6 mols.) and the reaction completed by 1 hours' boiling under reflux. The excess of thionyl chloride was removed under reduced pressure at 70—80°, and to the residual, pale yellow oil, saturated methyl-alcoholic ammonia (25 c.c.) was added at 0°. The solution was evaporated, the residual solid triturated with water to remove ammonium chloride, and the residue, crystallised from aqueous alcohol, gave a small yield of benzamido-*tert.*-butyl cyanide identical with that described above, m. p. and mixed m. p. 122°. Repetition of this experiment with only one mol. of thionyl chloride in benzene, and treatment of the crude acid chloride with aqueous (*d* 0·88) ammonia, gave 90% of β-benzamido-αα-dimethylpropionamide, m. p. 151°, identical with the benzoyl derivative of the amino-amide (see above).

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292. *Aliphatic Nitro-compounds. Part XIII. Preparation of 3-Nitro-1-arylalkyl Cyanides by Interaction of Arylmethyl Cyanides and α-Nitro-olefins.**

By G. D. Buckley, F. G. Hunt, and A. Lowe.

Arylmethyl cyanides, but not 1-arylethyl cyanides, react with α-nitro-olefins in presence of alkali alkoxides (preferably potassium *tert.*-amyloxide) to give 3-nitro-1-arylalkyl cyanides. 2-Nitroalkyl esters may be used in place of nitro-olefins, *e.g.*, 1-nitro-2-methylprop-1-ene or nitro*tert.*-butyl nitrate reacts with benzyl cyanide to give 3-*nitro*-1-*phenyl*-2 : 2-*dimethylpropyl cyanide* (II).

The use of α-nitro-olefins as the unsaturated component in reactions of the Michael type has been described in earlier parts in this series and elsewhere. Active methylene compounds which have been used successfully in such reactions include primary and secondary nitro-paraffins (Part VIII), ethyl malonate (Kohler *et al.*, *J. Amer. Chem. Soc.*, 1919, **41**, 764; 1926, **48**, 1770), and acetone (Hass and Riley, *Chem. Reviews*, 1943, **32**, 373), and this type of reaction has now been extended to the preparation of 3-nitro-1-arylalkyl cyanides by addition of arylmethyl cyanides to α-nitro-olefins.

$$Ar\cdot CH_2\cdot CN + CH_2{:}CH\cdot NO_2 \longrightarrow NO_2\cdot CH_2\cdot CH_2\cdot CHAr\cdot CN$$

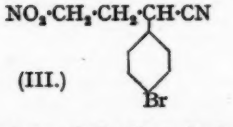
Benzyl cyanide reacted readily with 1-nitro-2-methylprop-1-ene in the presence of sodium methoxide to give 3-*nitro*-1-*phenyl*-2 : 2-*dimethylpropyl cyanide* (II) in 12% yield, but by using potassium *tert.*-amyloxide in place of the methoxide catalyst the yield was raised to 60%. From *p*-bromobenzyl cyanide and 1-naphthylmethyl cyanide, with the amyloxide catalyst, 3-*nitro*-1-p-*bromophenyl*-2 : 2-*dimethylpropyl cyanide* (III) and 3-*nitro*-1-(1-*naphthyl*)-2 : 2-*dimethylpropyl cyanide* (IV) were obtained in 48% and 70% yield respectively.

The adducts to 2-nitrobut-2-ene and 1-nitro*cyclo*hexene were obtained as viscous oils from which it was difficult to isolate the pure diastereoisomerides: thus, benzyl cyanide with 2-nitrobut-2-ene gave 3-*nitro*-1-*phenyl*-2-*methyl*-n-*butyl cyanide* (I) and *p*-bromobenzyl cyanide added to 1-nitro*cyclo*hexene to form 2-*nitro*-1-(p-*bromo*-α-*cyanobenzyl*)cyclo*hexane* (V) from which a crystalline isomer was isolated in small yield and with considerable difficulty. An attempt to add 1-phenylethyl cyanide (Meyer, *Annalen*, 1899, **250**, 123) to 1-nitro-2-methylprop-1-ene in the presence of potassium *tert.*-amyloxide failed.

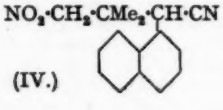
$NO_2\cdot CHMe\cdot CHMe\cdot CHPh\cdot CN$ (I.)

$NO_2\cdot CH_2\cdot CMe_2\cdot CHPh\cdot CN$ (II.)

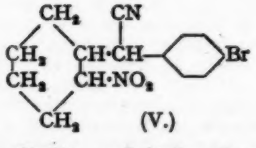
$NO_2\cdot CH_2\cdot CHMe\cdot CHPh\cdot CN$ (VI.)



(III.)



(IV.)



(V.)

Esters of 2-nitro-alcohols yield nitro-olefins on treatment with alkalis, and it has been shown that such esters can be used instead of nitro-olefins in addition reactions provided that sufficient alkali is present to neutralise the liberated acid. Nitro-*tert.*-butyl nitrate reacted with 2 mols. of the potassium salt of benzyl cyanide to give 3-nitro-1-phenyl-2 : 2-dimethylpropyl cyanide identical with the product obtained from 1-nitro-2-methylprop-1-ene, and under similar conditions 2-nitro*iso*propyl acetate gave 3-*nitro*-1-*phenyl*-2-*methylpropyl cyanide* (VI).

The reaction is of fairly general application for the preparation of 3-nitro-1-arylalkyl cyanides and is complementary to the method of preparation described in Part XIV of this series. The two methods in conjunction make possible the preparation of a wide variety of these hitherto inaccessible compounds.

Experimental.

Microanalyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

3-*Nitro*-1-*phenyl*-2-*methyl*-n-*butyl Cyanide* (I).—Benzyl cyanide (60 g.) was run into a solution of sodium methoxide [from sodium (12 g.) in methyl alcohol (200 c.c.)] at 20° and a solution of 2-nitrobut-2-ene (50 g.; this series, Part III) in methyl alcohol (100 c.c.) added dropwise during 1 hour at 5—10°. The mixture was heated at 60° for 18 hours, poured into water, and extracted with ether. The extract was washed with water and discarded, and the combined aqueous solutions were acidified

* Patent application pending.

with acetic acid (50 c.c.) and extracted with ether. The extract was dried and fractionated, giving the *cyanide* as a yellow oil (28·5 g.), b. p. 129—134°/0·2 mm. (Found: N, 13·15. $C_{12}H_{14}O_2N_2$ requires N, 12·85%).

3-*Nitro*-1-*phenyl*-2 : 2-*dimethylpropyl Cyanide* (II).—(a) *From* 1-*nitro*-2-*methylprop*-1-*ene*. To a stirred, ice-cooled solution of potassium *tert.*-amyloxide (from 8 g. of potassium), benzyl cyanide (23·5 g.) was added at 5—10°. 1-Nitro-2-methylprop-1-ene (20 g.; Levy and Scaife, in the press) was then added dropwise during 1 hour at 5—10°, and the reaction was completed by stirring at 60° for 2 hours. After cooling, the mixture was diluted with water and extracted with ether. The ethereal extract was washed with water and discarded, and the combined aqueous solutions were acidified with acetic acid (13 c.c.) and extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried, evaporated, and the residue (25 g.; 60% yield), consisting of almost pure 3-*nitro*-1-*phenyl*-2 : 2-*dimethylpropyl cyanide*, was left in a desiccator until completely solid. Crystallisation from a little methyl alcohol gave colourless needles, m. p. 59° (Found: C, 66·15; H, 5·95; N, 12·9. $C_{12}H_{14}O_2N_2$ requires C, 66·05; H, 6·4; N, 12·85%).

(b) *From nitro*-tert.-*butyl nitrate*. A solution of potassium *tert.*-amyloxide [from potassium (2 g.) in *tert.*-amyl alcohol (40 c.c.)] was treated with benzyl cyanide (5·85 g.) as before. Nitro-*tert.*-butyl nitrate (4·1 g.; Levy and Scaife, in the press) in *tert.*-amyl alcohol (5 c.c.) was added during 1 hour at 5—10°, and the mixture was then stirred at 60° for 2 hours and worked up as before. The product, m. p. 59°, was identical with that prepared above from 1-nitro-2-methylprop-1-ene.

3-*Nitro*-1-p-*bromophenyl*-2 : 2-*dimethylpropyl Cyanide* (III).—*p*-Bromobenzyl cyanide (9·8 g.) was brought into reaction with 1-nitro-2-methylprop-1-ene (5·05 g.) as described for benzyl cyanide. After several days in a desiccator the product solidified (7·1 g.; 48% yield), and crystallisation from methyl alcohol gave colourless needles of 3-*nitro*-1-p-*bromophenyl*-2 : 2-*dimethylpropyl cyanide*, m. p. 72—74° (Found: N, 9·4; Br, 27·55. $C_{12}H_{13}O_2N_2Br$ requires N, 9·4; Br, 26·9%).

3-*Nitro*-1-(1-*naphthyl*)-2 : 2-*dimethylpropyl Cyanide* (IV).—1-Naphthylmethyl cyanide (5 g.) was brought into reaction with 1-nitro-2-methylprop-1-ene (3 g.) as described for benzyl cyanide. The product (5·5 g.; 70% yield), isolated as before, solidified on removal of the ether. After two recrystallisations from alcohol (charcoal) the *cyanide* was obtained as long, colourless needles, m. p. 116° (Found: C, 71·7; H, 6·0; N, 10·4. $C_{16}H_{16}O_2N_2$ requires C, 71·65; H, 6·0; N, 10·4%).

3-*Nitro*-1-*phenyl*-2-*methylpropyl Cyanide* (VI).—A solution of potassium *tert.*-amyloxide [from potassium (8 g.) in *tert.*-amyl alcohol (160 c.c.)] was treated with benzyl cyanide (23·5 g.) as before. 2-Nitro*iso*propyl acetate (14·6 g.; Schmidt and Rutz, *Ber.*, 1928, **61**, 2142) was then added during 1 hour at 5—10°, and the resulting solution was stirred at 60° for 2 hours, cooled to 20°, and diluted with water. Isolation in the usual way yielded 3-*nitro*-1-*phenyl*-2-*methylpropyl cyanide* as a pale yellow oil (6·7 g.; 25% yield), b. p. 122—126°/0·15 mm. (Found: C, 65·3; H, 5·55; N, 14·2. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·75%).

2-*Nitro*-1-(p-*bromo*-α-*cyanobenzyl*)cyclo*hexane* (V).—1-Nitrocyclohexene (14 g.; Wieland *et al.*, *Annalen*, 1921, **424**, 71) was brought into reaction with *p*-bromobenzyl cyanide (21·6 g.) in presence of potassium *tert.*-amyloxide as previously described. The crude product, isolated as before, was a viscous oil (10·7 g.), apparently a mixture of diastereoisomers. After several days in a desiccator, it partly crystallised, and was then treated with a little alcohol and the crystals were collected (2·9 g.). Recrystallisation from methyl alcohol gave the *compound* as colourless granules, m. p. 103—104° (Found: N, 8·75; Br, 25·2. $C_{14}H_{15}O_2N_2Br$ requires N, 8·65; Br, 24·75%).

IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH LABORATORIES,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9. [*Received, January 23rd*, 1947.]

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293. *Aliphatic Nitro-compounds. Part XIV. Preparation of 3-Nitroalkyl Cyanides by Reaction of Nitro-paraffins with Unsaturated Cyanides.**

By G. D. BUCKLEY, T. J. ELLIOTT, F. G. HUNT, and A. LOWE.

A series of 3-nitroalkyl cyanides is prepared by the interaction of vinyl cyanide with primary and secondary nitro-paraffins in the presence of alkali. Both propenyl and allyl cyanide react with 1-nitropropane to give 3-*nitro*-2-*methyl*-n-*amyl cyanide* and with 2-nitropropane to give 3-*nitro*-2 : 3-*dimethyl*-n-*butyl cyanide*. α-Cyanostilbenes react with primary nitro-compounds in presence of secondary aliphatic amines to give 3-nitro-1 : 2-diarylalkyl cyanides, *e.g.*, α-cyanostilbene and nitromethane give 3-*nitro*-1 : 2-*diphenylpropyl cyanide* (VIII; R = H).

WHEN this work was carried out only two 3-nitroalkyl cyanides had been reported: 3-nitropropyl cyanide, prepared by Henry (*Bull. Acad. Sci. Belg.*, 1895, **36**, 152) by the action of silver nitrite on 3-iodopropyl cyanide, and nitrotris-(2-cyanoethyl)methane (I) prepared by Bruson and Reiner (*J. Amer. Chem. Soc.*, 1943, **65**, 23) by addition of nitromethane to vinyl cyanide (acrylonitrile). As large quantities of 3-nitroalkyl cyanides were required in connection with other investigations, we decided to extend the application of Bruson's method to other olefins and nitro-paraffins.

* Patent application pending.

Since our work was completed, Bruson (U.S.P. 2,361,259) has reported the addition of nitro-paraffins to vinyl cyanide in an inert solvent (*e.g.*, dioxan or *tert.*-butyl alcohol), preferably at about 40° and in the presence of a small amount of alkali such as sodium hydroxide or a quaternary ammonium base as catalyst. In this way nitromethane gave the tris-adduct (I), other primary nitro-paraffins gave mixtures of bis- (II) and mono-adducts (III), whereas secondary nitro-paraffins gave mono-adducts (IV).

$NO_2{\cdot}C(CH_2{\cdot}CH_2{\cdot}CN)_3$ (I.) $\quad R{\cdot}C(NO_2)(CH_2{\cdot}CH_2{\cdot}CN)_2$ (II.) $\quad R{\cdot}CH(NO_2){\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (III.)

$CR'R''(NO_2){\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (IV.) $\quad CH(NO_2)(CH_2{\cdot}CH_2{\cdot}CN)_2$ (V.)

We have found it more convenient to effect the addition by refluxing an alcoholic solution of the cyanide, nitro-paraffin, and catalyst for a short time. The yields of mono-adducts (type III) from primary nitro-paraffins are improved by using a full molecular proportion of alkali as condensing agent, and with this technique, the bis-adduct to nitromethane (V) has been obtained.

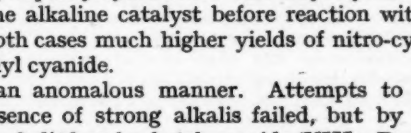
The following new 4-nitro-cyanides have been made by this method : 1-*nitro*-1-(2-*cyanoethyl*)-cyclo*hexane*, 3-*nitro*-4-*methoxy*-4-*phenyl*-3-*methyl*-n-*butyl cyanide* (VI), 3-*nitro*-5-n-*butylsulphonyl*-3-*methyl*-n-*amyl cyanide*, and 3-*nitro*-1 : 5-*dicyanopentane*. The known 3-nitro-3-methyl-*n*-butyl cyanide and 3-nitro-*n*-butyl cyanide (cf. Bruson, *loc. cit.*) have been prepared by the modified method : the first of these has been converted into its *iminoethyl ether* and *amidine hydrochloride*, and the second has been hydrolysed with acid to 3-keto-*n*-butyl cyanide (lævulonitrile).

The general method of addition has been extended by the use of substituted vinyl cyanides. Thus 2-nitropropane reacted with *iso*propenyl cyanide (methacrylonitrile) in presence of a little methyltriethylammonium hydroxide to give 3-*nitro*-1 : 3-*dimethyl*-n-*butyl cyanide* and with propenyl cyanide (crotononitrile) to give the isomeric 3-*nitro*-2 : 3-*dimethyl*-n-*butyl cyanide*, which was also formed by interaction of allyl cyanide and 2-nitropropane. Similarly, both propenyl and allyl cyanide reacted with 1-nitropropane to give 3-*nitro*-2-*methyl*-n-*amyl cyanide* (VII), the identity of the products being established by hydrolysis to 3-keto-2-methyl-*n*-amyl cyanide, which was characterised as the 2 : 4-*dinitrophenylhydrazone*. The allyl cyanide was presumably isomerised to propenyl cyanide by the alkaline catalyst before reaction with the nitro-paraffin, but a curious feature was that in both cases much higher yields of nitro-cyanide were obtained from allyl cyanide than from propenyl cyanide.

Aryl substituted vinyl cyanides behaved in an anomalous manner. Attempts to cause nitroethane to react with α-cyanostilbene in presence of strong alkalis failed, but by using a secondary aliphatic amine as catalyst 3-*nitro*-1 : 2-*diphenyl*-n-*butyl cyanide* (VIII; R = Me) was produced in 60% yield.

$NO_2{\cdot}CHR{\cdot}CHPh{\cdot}CHPh{\cdot}CN$ (VIII.)

$NO_2{\cdot}CHMe{\cdot}CHPh{\cdot}CH(CN)$–C$_6H_4$–Br (IX.)



(X.)

Similarly, nitromethane gave one of the isomerides of 3-*nitro*-1 : 2-*diphenyl*-n-*propyl cyanide* (VIII; R = H), and nitroethane reacted with 4-bromo-α-cyanostilbene to give one of the isomerides of 3-*nitro*-2-*phenyl*-1-p-*bromophenyl*-n-*butyl cyanide* (IX), but all attempts to cause secondary nitro-paraffins to react with α-cyanostilbene were unsuccessful. Methyl 2-nitroethyl ether reacted with α-cyanostilbene in the presence of piperidine, but unexpectedly the product was acid-soluble, the methoxyl group having been replaced by a piperidine residue to give 3-*nitro*-4-*piperidino*-1 : 2-*diphenyl*-n-*butyl cyanide* (X).

In many of the above products (IV), (VII), (VIII), (IX), and (X) there is more than one asymmetric carbon atom, so that the compounds would be expected to be formed as mixtures of stereoisomerides. In these cases, only one isomer has been identified and no attempt has been made to isolate the other stereoisomerides : the yields recorded therefore do not necessarily indicate the extent of the reaction.

Experimental.

Microanalyses are by Mr. E. S. Morton. M. ps. are uncorrected.

3-*Nitro*-3-*methyl*-n-*butyl Cyanide*.—Aqueous potassium hydroxide (10 c.c. of 33%) was added to a solution of 2-nitropropane (261 g.) in alcohol (750 c.c.), which was then heated to boiling. Vinyl cyanide

(159 g.) was run into the stirred solution at such a rate that the mixture refluxed gently. After a further 1 hour's refluxing, the solution was cooled, made just acid to Congo-red by addition of 20% sulphuric acid, stirred with barium carbonate to remove excess of acid, and filtered. The filtered solution was fractionated to give the cyanide as a colourless oil (330 g.), b. p. 70°/0·09 mm. (Bruson, *loc. cit.*, gives b. p. 105—107°/1 mm.) (Found: C, 50·55; H, 7·0; N, 19·7. Calc. for $C_6H_{10}O_2N_2$: C, 50·7; H, 7·05; N, 19·7%). The *iminoethyl ether hydrochloride*, prepared by passing dry hydrogen chloride into an alcoholic solution of the cyanide below 20°, had m. p. 108° (Found: N, 11·75; Cl, 16·2. $C_6H_{11}O_2N_2$,HCl requires N, 12·4; Cl, 15·8%). The *amidine hydrochloride*, prepared by the action of alcoholic ammonia on the iminoethyl ether hydrochloride, had m. p. 214° (Found: Cl, 18·4. $C_6H_{12}O_2N_2$,HCl requires Cl, 18·15%).

1-*Nitro*-1-(2-*cyanoethyl*)cyclo*hexane*.—Nitro*cyclo*hexane (43 g.) was brought into reaction with vinyl cyanide (18 g.) as described for 2-nitropropane. Distillation gave the *product* as a pale yellow oil (24 g.), b. p. 98—108°/0·15 mm., which from light petroleum (b. p. 40—60°) gave colourless needles, m. p. 42° (Found: C, 59·9; H, 7·45; N, 15·25. $C_9H_{14}O_2N_2$ requires C, 59·35; H, 7·7; N, 15·4%).

3-*Nitro*-1 : 2-*dimethyl*-n-*butyl Cyanide*.—(*a*) 2-Nitropropane (6·65 g.), allyl cyanide (5·0 g.), ethyl alcohol (50 c.c.), and aqueous methyltriethylammonium hydroxide (2·7 c.c. of 37%) were refluxed for 20 hours. The product (9·45 g.; 80%), isolated as in the previous cases, was a colourless oil, b. p. 86—87°/0·24 mm. (Found: C, 54·5; H, 7·8; N, 17·55. $C_7H_{12}O_2N_2$ requires C, 53·85; H, 7·7; N, 17·95%).

(*b*) The above experiment was repeated using propenyl cyanide in place of allyl cyanide. A colourless oil, b. p. 86—87°/0·24 mm., was isolated in 55% yield (Found: N, 18·25%).

3-*Nitro*-1 : 2-*dimethyl*-n-*butyl Cyanide*.—2-Nitropropane (8·9 g.) was brought into reaction with *iso*propenyl cyanide (7·0 g.) as described above for propenyl cyanide. After isolation as before, the crude product was distilled, giving the *cyanide* (6·3 g.), b. p. 65°/0·08 mm., m. p. 51—53° (from alcohol) (Found: C, 53·5; H, 7·35; N, 17·7. $C_7H_{12}O_2N_2$ requires C, 53·85; H, 7·7; N, 17·95%).

3-*Nitro*-4-*methoxy*-4-*phenyl*-3-*methyl*-n-*butyl Cyanide*.—Aqueous sodium hydroxide (5 c.c. of 32%) and vinyl cyanide (37·5 g.) were added to a solution of methyl 2-nitro-1-phenylpropyl ether (48·5 g.; this series, Part III) in dioxan (100 c.c.), and the mixture was stirred at 20° for 18 hours. The solution was poured into water, acidified with hydrochloric acid, and extracted with chloroform. Fractionation of the extract gave the *product* as a colourless oil (50 g.), b. p. 163—167°/0·5 mm. (Found: C, 62·5; H, 6·3; N, 11·3. $C_{13}H_{16}O_3N_2$ requires C, 62·9; H, 6·45; N, 11·3%).

3-*Nitro*-5-n-*butylsulphonyl*-3-*methyl*-n-*amyl Cyanide*.—Vinyl cyanide (1·05 g.) and methyltriethylammonium hydroxide (0·75 c.c. of 37%) were added to a solution of 3-nitrodibutyl sulphone (4·2 g.; this series, Part XVII) in alcohol (20 c.c.), which was then refluxed for 3 hours, cooled, and poured into water (250 c.c.). The mixture was extracted with ether and the extract was washed with dilute aqueous sodium hydroxide, dried, and the solvent removed to yield the *cyanide* as a very viscous brown oil, which could not be distilled or induced to crystallise (Found: N, 9·9; S, 11·4. $C_{11}H_{20}O_4N_2S$ requires N, 10·5; S, 11·6%).

4-*Nitro*-n-*butyl Cyanide*.—A solution of sodium methoxide [from sodium (11·5 g.) and methyl alcohol (150 c.c.)] was slowly run into a stirred solution of nitroethane (38 g.) in methyl alcohol (75 c.c.) at 0—10°. Vinyl cyanide (27 g.) was slowly added at 20—25°; during the addition the white precipitate of the sodium salt of nitroethane dissolved. The mixture was then acidified with acetic acid (32 g.), the solvent removed under reduced pressure at 40°, and the residue diluted with sufficient water to dissolve the sodium acetate and extracted with ether. The extract was dried and fractionated to give the cyanide as a colourless oil (19 g.), b. p. 82—84°/0·25 mm. (Bruson, *loc. cit.*, gives b. p. 107—110°/2 mm.) (Found: N, 21·65. Calc. for $C_5H_8O_2N_2$: N, 21·85%).

3-*Keto*-n-*butyl Cyanide*.—3-Nitro-*n*-butyl cyanide (13 g.) was dissolved in alcohol (10 c.c.) and aqueous sodium hydroxide (8 c.c. of 32%) was added at 10—15°. The resulting solution was diluted with water (30 c.c.) and run into dilute sulphuric acid (70 c.c. of 30%) at 10—15°. After being stirred for a further 15 minutes the mixture was extracted with ether. The extract was dried and fractionated to give the ketone as a colourless oil, b. p. 98—102°/9 mm. The 2 : 4-*dinitrophenylhydrazone* formed orange leaflets, m. p. 146°, from 2-ethoxyethyl alcohol (Found: C, 47·55; H, 4·05; N, 25·25. $C_{11}H_{11}O_4N_5$ requires C, 47·65; H, 4·0; N, 25·25%).

3-*Nitro*-2-*methyl*-n-*amyl Cyanide*.—(*a*) 1-Nitropropane (8·9 g.) was added dropwise to a solution of potassium hydroxide (5·6 g.) in alcohol (20 c.c.), the temperature being kept below 10°. The solution was then stirred at 50° and a solution of allyl cyanide (6·7 g.) in alcohol (30 c.c.) was added dropwise. The solution was stirred at 50° for 18 hours, cooled, and neutralised by dropwise addition of 5N-sulphuric acid, followed by treatment with barium carbonate. The filtered solution was fractionated, giving 3-nitro-2-methyl-*n*-amyl cyanide as a colourless oil (12·5 g.; 80% yield), b. p. 76°/0·1 mm.

The oil (1 g.), dissolved in a solution of sodium hydroxide (0·5 g.) in alcohol (5 c.c.) and water (5 c.c.), was added dropwise to ice-cold sulphuric acid (10 c.c. of 30%) and the mixture poured into excess of a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. After standing overnight the precipitate was collected and crystallised from alcohol, giving 3-*keto*-2-*methyl*-n-*amyl cyanide* 2 : 4-*dinitrophenylhydrazone* as orange needles, m. p. 103—104° (Found: C, 51·25; H, 4·7; N, 23·25. $C_{13}H_{15}O_4N_5$ requires C, 51·15; H, 4·9; N, 22·95%).

(*b*) The above experiment was repeated using propenyl cyanide in place of allyl cyanide. This gave the nitro-cyanide in 35% yield as a colourless oil, b. p. 74—75°/0·09 mm. Hydrolysis and reaction with 2 : 4-dinitrophenylhydrazine as before gave a product, m. p. 102—103°, identical with the 2 : 4-dinitrophenylhydrazone described in (*a*) above (Found: N, 22·95%).

3-*Nitro*-1 : 5-*dicyanopentane*.—A solution of sodium methoxide [from sodium (7·5 g.) and methyl alcohol (150 c.c.)] was added dropwise to a stirred solution of nitromethane (20 g.) in methyl alcohol (75 c.c.) at 0—10°, and vinyl cyanide (32 g.) added during 1 hour. The mixture was treated with acetic acid (20 g.), concentrated under reduced pressure, and the residue diluted with water (300 c.c.) and shaken with ether, which caused the separation of crystals. Repeated recrystallisation from alcohol (charcoal) gave colourless needles (4 g.) of 3-*nitro*-1 : 5-*dicyanopentane*, m. p. 63° (Found: C, 50·2; H, 5·4; N, 24·95. $C_7H_9O_2N_3$ requires C, 50·3; H, 5·4; N, 25·1%).

3-*Nitro*-1 : 5-*dicyano*-3-p-*bromophenylpentane*.—Methyltriethylammonium hydroxide (1 c.c. of 37%) was added to a solution of *p*-bromophenylnitromethane (4·3 g.) and vinyl cyanide (1·6 g.) in *tert.*-butyl alcohol (50 c.c.). Next day, the precipitate was collected (1·7 g.) and recrystallised repeatedly from alcohol, giving the dicyanide as colourless needles, m. p. 138—139° (Found: N, 13·2; Br, 24·45. Calc. for $C_{13}H_{12}O_2N_2Br$: N, 13·05; Br, 24·85%).

3-*Nitro*-1 : 2-*diphenyl*-n-*butyl Cyanide* (III; R = Me).—α-Cyanostilbene (205 g.), nitroethane (75 g.), and diethylamine (100 c.c.) were heated at 35—40° until a clear solution resulted. On being kept overnight, the mixture solidified. After crystallisation, first from alcohol and then from 2-ethoxyethyl alcohol, the *cyanide* was obtained as colourless crystals (160 g.), m. p. 164—165° (Found: C, 72·3; H, 5·7; N, 10·1. $C_{17}H_{16}O_2N_2$ requires C, 72·85; H, 5·7; N, 10·0%).

3-*Nitro*-4-*piperidino*-1 : 2-*diphenyl*-n-*butyl Cyanide* (X).—α-Cyanostilbene (2·7 g.) was brought into reaction with methyl 2-nitroethyl ether (2·4 g.) in the presence of piperidine (1·75 g.) as described above for nitroethane. The *product* was collected, washed with methyl alcohol, and recrystallised repeatedly from acetone, giving colourless needles (2·9 g.), m. p. 171° (Found: C, 72·1; H, 6·65; N, 11·7. $C_{22}H_{25}O_2N_2$ requires C, 72·7; H, 6·9; N, 11·6%). The product was soluble in dilute acid and was reprecipitated unchanged by addition of sodium hydroxide.

3-*Nitro*-1 : 2-*diphenyl*-n-*propyl Cyanide* (VIII; R = H).—α-Cyanostilbene (38·5 g.), nitromethane (15 g.), and diethylamine (20 c.c.) were heated at 50° until a homogeneous solution resulted. After several days at 20°, the crystalline precipitate was collected, washed with ether, and recrystallised from alcohol, giving the *cyanide* as colourless prisms (5·5 g.), m. p. 94—96° (Found: N, 10·55. $C_{16}H_{14}O_2N_2$ requires N, 10·55%).

3-*Nitro*-2-*phenyl*-1-p-*bromophenyl*-n-*butyl Cyanide* (XIV).—Nitroethane (1·65 g.), 4-bromo-α-cyanostilbene (5·7 g.; Frost, *Annalen*, 1889, **250**, 161) and piperidine (1·75 g.) were mixed and kept at 20° for 3 days. The semi-solid mass was then dissolved in hot methyl alcohol (10 c.c.) and allowed to cool. The crystalline product was collected (3·35 g.) and purified by repeated recrystallisation from alcohol, giving colourless crystals of the *cyanide*, m. p. 187—189° (Found: C, 56·65; H, 4·2; N, 8·05; Br, 21·75. $C_{17}H_{15}O_2N_2Br$ requires C, 56·8; H, 4·2; N, 7·8; Br, 22·3%).

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294. *Aliphatic Nitro-compounds. Part XV. Preparation of Heterocyclic Bases by Reduction of 3-Nitroalkyl Cyanides.**

By G. D. BUCKLEY and T. J. ELLIOTT.

Reduction of 3-nitro-3-methyl-*n*-butyl cyanide (I) with iron and hydrochloric acid gives a mixture of 5-amino-2 : 2-dimethylpyrroline *N*-oxide (II) [or its tautomeride (II*a*)], with 5-amino-2 : 2-dimethylpyrrolidine (III) [or its tautomeride (III*a*)]. The structure of (III) is established by formation from it of mono- and di-benzoyl derivatives, and by its hydrolysis to 5 : 5-dimethyl-2-pyrrolidone (V) by water and Raney nickel. The structure of the *N*-oxide (II) follows from its reduction to (III) by zinc-dust distillation and to 2 : 2-dimethylpyrrolidine (IV) on catalytic hydrogenation. Similar reactions with analogues of (I) are described, and possible mechanisms are discussed.

WITH a view to the synthesis of 3-amino-3-methyl-*n*-butyl cyanide, 3-nitro-3-methyl-*n*-butyl cyanide (I) was reduced with iron and hydrochloric acid. Two products were obtained: (*a*) a crystalline solid, $C_6H_{12}ON_2$, m. p. 238° (17% yield), and (*b*) a crystalline volatile base, $C_6H_{12}N_2$, (30% yield), with a formula and equivalent weight in agreement with those of the expected amino-cyanide, but with properties which excluded this structure.

The base, $C_6H_{12}N_2$, with 0·5 mol. of benzoyl chloride in ether gave a weakly basic monobenzoyl derivative which formed a picrate and was precipitated unchanged from its hydrochloric acid solution by addition of ammonia.

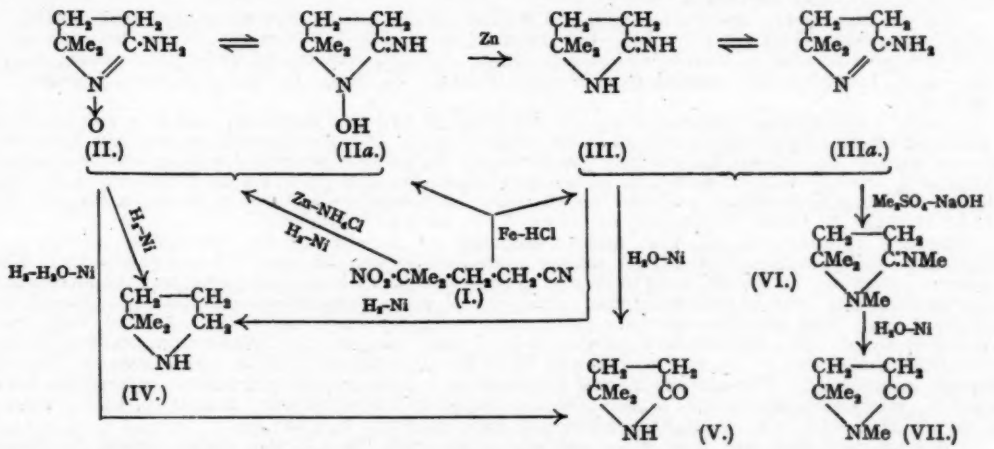
Benzoylation with excess of benzoyl chloride (Schotten–Baumann) gave both the *monobenzoyl* derivative and an acid-insoluble *dibenzoyl* derivative. This suggested that the base was the internal amidine 5-*imino*-2 : 2-*dimethylpyrrolidine* (III) [or 5-amino-2 : 2-dimethylpyrroline (III*a*)]. This was confirmed by the behaviour of the base on hydrolysis, reduction, and methylation. It was extremely resistant to acid or alkaline hydrolysis, but on boiling it with water in the presence of a little Raney nickel, ammonia was evolved and a crystalline, water-soluble solid $C_6H_{11}ON$, having the expected properties of 2 : 2-*dimethyl*-5-*pyrrolidone* (V), was formed. Reduction of the imine (III) with sodium and alcohol was difficult, but gave a small yield of 2 : 2-*dimethylpyrrolidine* (IV), also formed in good yield by catalytic reduction at 100°/100 atms. with Raney nickel under anhydrous conditions. Methylation of (III) with methyl sulphate and sodium hydroxide gave a dimethyl derivative, shown to be 5-*methylimino*-1 : 2 : 2-*trimethylpyrrolidine* (VI), by hydrolysis with water and Raney nickel to methylamine

* Patent application pending.

and 1 : 2 : 2-*trimethyl*-5-*pyrrolidone* (VII). The evidence in favour of the internal amidine structure (III) or (III*a*) is therefore conclusive.

Attention was then directed to the structure of the base $C_6H_{12}ON_2$ (above). This material was the main product when 3-nitro-3-methyl-*n*-butyl cyanide (I) was reduced with zinc dust and ammonium chloride under conditions which normally would be expected to reduce an aliphatic nitro-compound to the hydroxylamine, and was formed in 75% yield by reduction of (I) with hydrogen and Raney nickel at ordinary temperature and pressure. The base was weak; it gave a hydrochloride but would not react with benzoyl chloride, acetic anhydride, phenyl *iso*cyanate, or *N*-nitro-*N'*-2 : 4-dinitrophenylurea. It contained two active hydrogen atoms (Zerewitinoff). Distillation with zinc dust gave the iminopyrrolidine (III), and reduction with sodium and alcohol gave a mixture of (III) and 2 : 2-dimethylpyrrolidine (IV). The latter was also formed by catalytic hydrogenation of the base $C_6H_{12}ON_2$ under anhydrous conditions at 100°/100 atms., but in the presence of water the pyrrolidone (V) was obtained in good yield, presumably by hydrolysis of the first-formed imine (III). Attempts to hydrolyse the base itself by boiling it with water and Raney nickel were unsuccessful.

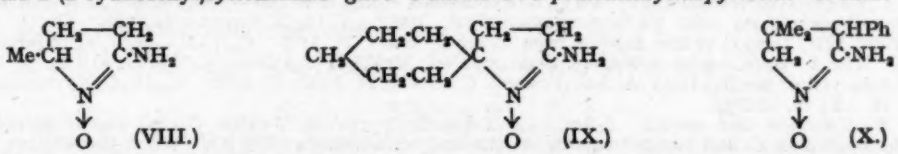
On this evidence the compound was formulated as 5-*amino*-2 : 2-*dimethylpyrroline* N-*oxide* (II) [or the tautomeric 5-*imino*-1-*hydroxy*-2 : 2-*dimethylpyrrolidine* (II*a*)], and its formation is ascribed to cyclisation of the first-formed 3-hydroxylamino-3-methyl-*n*-butyl cyanide. A similar case has been reported by Bauer (*Ber.*, 1938, **71**, 2226), who hydrogenated *o*-nitrostyryl cyanide over a palladium catalyst and obtained 2-aminoquinoline *N*-oxide in 60% yield.



In the reduction of the nitro-cyanide (I) with iron and hydrochloric acid, the iminopyrrolidine (III) might be formed either by reduction of the *N*-oxide (II) or by reduction of the nitro-cyanide to amino-cyanide, followed by cyclisation. Although difficult to prove conclusively, the former appears to be the more probable route; a careful search failed to reveal any amino-cyanide in the reduction products of (I), and it has been shown that the *N*-oxide (II) is, in fact, slowly reduced to the iminopyrrolidine (III) by iron and hydrochloric acid.

Attempts to reduce 3-nitro-3-methyl-*n*-butyl cyanide with platinum or palladium catalysts in the presence of mineral acids were unsuccessful, and use of stannous chloride and hydrochloric acid resulted in hydrolysis. It was concluded, therefore, that the preparation of 3-amino-3-methyl-*n*-butyl cyanide by reduction of the nitro-cyanide was impracticable.

Analogues of (I) were obtained, usually in good yield, by catalytic reduction of other 3-nitroalkyl cyanides. 3-Nitro-*n*-butyl cyanide gave 5-*amino*-2-*methylpyrroline* N-*oxide* (VIII), 1-nitro-1-(2-cyanoethyl)*cyclo*hexane gave 5-*amino*-2 : 2-*pentamethylenepyrroline* N-*oxide* (IX),



and 3-nitro-1-phenyl-2 : 2-dimethyl-*n*-propyl cyanide gave 2-*amino*-3-*phenyl*-4 : 4-*dimethylpyrroline* N-*oxide* (X). Results of hydrogenations at 100 atms. were similar to those obtained

at atmospheric pressure. Raney nickel and palladised calcium carbonate appeared to be equally effective as catalysts, but Adams's platinum oxide gave inferior yields.

Experimental.

Analyses are by Mr. E. S. Morton. M. ps. are uncorrected. The nitro-cyanides were prepared by the methods described in Parts XIII and XIV of this series.

Reduction of 3-*Nitro*-3-*methyl*-n-*butyl Cyanide.*—(a) *With iron and hydrochloric acid.* Iron filings (30—60 mesh) (70 g.), water (150 c.c.), and hydrochloric acid (20 c.c. of 35%) were stirred together until the solution was no longer acid to Congo-red. The mixture was then heated to 100° and a solution of 3-nitro-3-methyl-*n*-butyl cyanide (47·5 g.) in alcohol (100 c.c.) was run in during 1 hour. The mixture was stirred and refluxed for 18 hours, cooled, and the filtered solution acidified to Congo-red with hydrochloric acid. The alcohol was distilled under reduced pressure, the residue diluted with sufficient water to dissolve the salts, and washed with ether. The aqueous solution was made strongly alkaline with potassium hydroxide and extracted repeatedly with ether (see later). The aqueous alkaline solution was then treated with solid potassium hydroxide and the precipitate collected and dissolved in a little water. Dilute hydrochloric acid was added until the solution was no longer alkaline to Clayton-yellow, and, after evaporation under reduced pressure, the product was isolated by extraction with absolute alcohol, evaporation of the extract and treatment with acetone giving 5-*amino*-2 : 2-*dimethylpyrroline* N-*oxide* (II) (8·0 g.) as a crystalline solid, which separated from alcohol–acetone in colourless plates, m. p. 238° (Found : C, 56·35; H, 9·45; N, 22·15. $C_6H_{12}ON_2$ requires C, 56·25; H, 9·4; N, 21·9%). The product was very soluble in water, chloroform, and alcohol, insoluble in ether, acetone, ethyl acetate, dioxan, and hydrocarbons. The *hydrochloride* had m. p. 173° (Found : Cl, 21·75. $C_6H_{12}ON_2,HCl$ requires Cl, 21·6%). The *picrate*, m. p. 160°, formed yellow needles from alcohol (Found : N, 20·0. $C_6H_{12}ON_2,C_6H_3O_7N_3$ requires N, 19·6%).

The ethereal extract was dried (KOH) and distilled, giving 5-*imino*-2 : 2-*dimethylpyrrolidine* (III) as colourless crystals (14·4 g.), b. p. 108—110°/15 mm., m. p. 73—74° [Found : *M* (by titration with 0·1N-hydrochloric acid to bromophenol-blue), 113·2. $C_6H_{12}N_2$ requires *M*, 112]. The *picrate*, m. p. 203—204°, formed yellow needles from alcohol (Found : N, 20·4. $C_6H_{12}N_2,C_6H_3O_7N_3$ requires N, 20·55%).

A solution of benzoyl chloride (0·6 g.) in dry ether (5 c.c.) was cautiously added to a solution of 5-imino-2 : 2-dimethylpyrrolidine (1 g.) in dry ether (5 c.c.). A vigorous reaction occurred, and after evaporation of the solvent the product was extracted with dilute aqueous ammonia and crystallised from 50% aqueous alcohol, giving the *monobenzoyl* derivative (0·6 g.) as colourless prisms, m. p. 98°, soluble in dilute hydrochloric acid and reprecipitated unchanged by addition of ammonia (Found : C, 72·0; H, 7·15; N, 12·65. $C_{13}H_{16}ON_2$ requires C, 72·2; H, 7·4; N, 12·95%).

Benzoyl chloride (6 g.) was added dropwise to a stirred and ice-cooled mixture of 5-imino-2 : 2-dimethylpyrrolidine (2 g.), sodium hydroxide (3·2 g.), and water (25 c.c.) at 10—15°. The mixture was stirred at 10—20° until the excess of benzoyl chloride had decomposed, and the precipitate was then collected, washed with water, and extracted with cold N-hydrochloric acid (50 c.c.). Treatment of the extract with aqueous ammonia precipitated a monobenzoyl derivative, identical with that described above. The acid-insoluble portion (3·2 g.) was repeatedly crystallised from acetone, giving colourless needles (0·3 g.), m. p. 179° (Found : C, 69·75; H, 5·65; N, 9·05%). This material was not further investigated. The acetone mother liquors were evaporated and the residue crystallised from alcohol, giving colourless needles of 5-*benzimido*-1-*benzoyl*-2 : 2-*dimethylpyrrolidine*, m. p. 133° (Found : C, 74·65; H, 6·6; N, 8·7. $C_{20}H_{20}O_2N_2$ requires C, 75·0; H, 6·25; N, 8·75%).

(b) *With zinc dust and ammonium chloride.* Zinc dust (25 g.) was added during 2½ hours to a vigorously stirred mixture of 3-nitro-3-methyl-*n*-butyl cyanide (20 g.), ammonium chloride (6 g.), and water (80 c.c.) at 10—15°. When reaction was complete the solution was filtered, neutralised with hydrochloric acid, evaporated under reduced pressure, and the residue extracted with absolute alcohol; the extract on dilution with dry ether gave the hydrochloride, m. p. 173°, of 5-amino-2 : 2-dimethylpyrroline *N*-oxide, from which the base, m. p. 238°, was obtained by basification.

(c) *Catalytically.* 3-Nitro-3-methyl-*n*-butyl cyanide (150 g.), dissolved in methyl alcohol (1500 c.c.), was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption of hydrogen ceased. The filtered solution was concentrated, finally by heating at 100°/20 mm., and the residue treated with acetone, giving 5-amino-2 : 2-dimethylpyrroline *N*-oxide. A second crop was obtained by concentrating the mother liquor and again treating the residue with acetone. The total yield was 101 g. (75%).

Reduction of 5-*Amino*-2 : 2-*dimethylpyrroline* N-*Oxide.*—(a) *Catalytically.* A solution of 5-amino-2 : 2-dimethylpyrroline *N*-oxide (10 g.) in anhydrous methanol (100 c.c.) was stirred with hydrogen and water and Raney nickel (1 g.) in an autoclave at 100°/100 atms. until absorption was complete, cooled, filtered from catalyst, and steam-distilled until free from volatile bases. The distillate was acidified with hydrochloric acid and evaporated to dryness. The hydrochloride was treated with a large excess of 40% aqueous potassium hydroxide, the base extracted with ether, the extract dried (KOH), and fractionated, giving 2 : 2-*dimethylpyrrolidine* (IV) (4·9 g.) as a colourless liquid, b. p. 105—106 (Found : *M* (by titration with 0·1N-hydrochloric acid to bromophenol-blue), 100·2. $C_6H_{13}N$ requires *M*, 99). The *picrate*, m. p. 190—191°, formed yellow needles from water (Found : N, 17·5. $C_6H_{13}N,C_6H_3O_7N_3$ requires N, 17·1%). The 2 : 4-*dinitrophenylcarbamyl* derivative (cf. McVeigh and Rose, *J.*, 1945, 621), m. p. 131°, formed long yellow needles from alcohol (Found : C, 50·65; H, 5·25; N, 18·2. $C_{13}H_{16}O_5N_4$ requires C, 50·65; H, 5·2; N, 18·2%).

(b) *With sodium and alcohol.* 5-Amino-2 : 2-dimethylpyrroline *N*-oxide (75 g.) was dissolved in absolute alcohol (2 l.) and treated rapidly at the boil with sodium (170 g.). When the sodium was completely dissolved, the solution was cooled and cautiously acidified to Congo-red with concentrated hydrochloric acid, filtered from salt and steam-distilled. The residual solution was diluted with an equal volume of 32% aqueous sodium hydroxide and extracted with ether. The extract, after drying

and distillation, yielded 5-imino-2 : 2-dimethylpyrrolidine (14·2 g.). The steam-distillate was acidified with hydrochloric acid and evaporated to dryness, leaving a hydrochloride, which, after basification and distillation, yielded 2 : 2-dimethylpyrrolidine (7·2 g.).

(c) *By distillation with zinc dust.* 5-Amino-2 : 2-dimethylpyrroline *N*-oxide (30 g.) was mixed thoroughly with zinc dust (30 g.) and heated, 20 g. at a time, in a distillation apparatus under 20 mm. The bath was heated to 280° and the temperature was then slowly raised to 320° and held at this until distillation ceased. The distillate was extracted with ether and the extract dried (KOH) and fractionated giving 5-imino-2 : 2-dimethylpyrrolidine (7 g.), b. p. 106°/15 mm.

(d) *With iron and hydrochloric acid.* 5-Amino-2 : 2-dimethylpyrroline *N*-oxide (20 g.) was reduced for 48 hours at 95—100° with iron (35 g.) and hydrochloric acid as described above for the reduction of the nitro-cyanide. Isolation as before gave 5-imino-2 : 2-dimethylpyrrolidine (7·9 g.), together with much unchanged starting materials.

Reduction of 5-Imino-2 : 2-dimethylpyrrolidine.—(a) *Catalytically.* The base (5 g.) was hydrogenated at 100°/100 atms. under anhydrous conditions as described above for 5-amino-2 : 2-dimethylpyrroline *N*-oxide. The resulting solution was filtered and fractionated, giving 2 : 2-dimethylpyrrolidine (IV) (3·8 g.); picrate, m. p. 190—191°.

(b) *With sodium and alcohol.* 5-Imino-2 : 2-dimethylpyrrolidine (7 g.) was reduced with sodium (50 g.) and absolute alcohol (600 c.c.) as described above for the pyrroline oxide. The product was worked up as before to give a small amount of 2 : 2-dimethylpyrrolidine, together with unchanged 5-imino-2 : 2-dimethylpyrrolidine (3·2 g.).

2 : 2-*Dimethyl-5-pyrrolidone* (V).—(*a*) A solution of 5-imino-2 : 2-dimethylpyrrolidine (3 g.) in water (30 c.c.) was stirred and refluxed for 3 hours with Raney nickel (0·1 g.); ammonia was evolved. The filtered solution was distilled, giving 2 : 2-*dimethyl-5-pyrrolidone* (2·1 g.) as colourless, hygroscopic crystals, m. p. 42°, b.p. 140°/20 mm. (Found : C, 63·4; H, 9·7; N, 12·15. $C_6H_{11}ON$ requires C, 63·7; H, 9·75; N, 12·4%). The *hydrochloride* had m. p. 150—152° (Found : Cl, 23·4. $C_6H_{11}ON,HCl$ requires Cl, 23·75%).

(*b*) 5-Amino-2 : 2-dimethylpyrroline *N*-oxide (5 g.), dissolved in methyl alcohol (100 c.c.), was stirred with Raney nickel and hydrogen at 100°/100 atms. until absorption of hydrogen ceased. Distillation of the product gave 2 : 2-dimethyl-5-pyrrolidone (3·2 g.).

Methylation of 5-Imino-2 : 2-dimethylpyrrolidine.—Methyl sulphate (40 g.) was added dropwise to a stirred and cooled mixture of 5-imino-2 : 2-dimethylpyrrolidine (10 g.) and aqueous sodium hydroxide (80 c.c. of 16%) at 10—15°. The mixture was stirred at 10—20° until the excess of methyl sulphate had decomposed, and was then treated with an equal volume of 32% sodium hydroxide solution and extracted with ether. The extract was dried (KOH) and distilled, giving *5-methylimino-1 : 2 : 2-trimethylpyrrolidine* (VI) (11 g.) as a colourless oil, b. p. 97—98°/18 mm. The *picrate*, m. p. 125°, formed yellow needles from water (Found : C, 46·2; H, 5·1; N, 19·25. $C_8H_{16}N_2,C_6H_3O_7N_3$ requires C, 45·55; H, 5·15; N, 19·0%).

1 : 2 : 2-*Trimethyl-5-pyrrolidone* (VII).—The base (above) (6·8 g.) in water (70 c.c.) was boiled with Raney nickel for 3 hours. An aqueous solution of the evolved gases was shown to be free from ammonia (no precipitate with Nessler's reagent), but, on boiling with *N*-nitro-*N'*-2 : 4-dinitrophenylurea, gave *N*-2 : 4-dinitrophenyl-*N'*-methylurea, m. p. and mixed m. p. with an authentic specimen, 204° (cf. McVeigh and Rose, *loc. cit.*). The aqueous residue was filtered from catalyst and distilled, giving 1 : 2 : 2-*trimethyl-5-pyrrolidone* (VII) (4·9 g.), as a colourless oil, b. p. 130°/60 mm. (Found : C, 66·2; H, 10·2; N, 10·95. $C_7H_{13}ON$ requires C, 66·1; H, 10·25; N, 11·05%).

5-Amino-2-methylpyrroline N-Oxide (VIII).—3-Nitro-*n*-butyl cyanide (32 g.) in methyl alcohol (400 c.c.) was hydrogenated in the presence of Raney nickel at 20°/1 atm. The filtered solution was concentrated and the residue was stirred with acetone and the solid collected (5 g.). Crystallisation from chloroform–acetone gave colourless, hygroscopic needles, m. p. 206° (Found : C, 52·65; H, 8·4; N, 24·3. $C_5H_{10}ON_2$ requires C, 52·65; H, 8·75; N, 24·55%).

5-Amino-2 : 2-pentamethylenepyrroline N-Oxide (IX).—1-Nitro-1-(2-cyanoethyl)*cyclo*hexane (21 g.) was hydrogenated and the product (8 g.) isolated as described above. Crystallisation from acetone–alcohol gave the *base* as colourless leaflets, m. p. 206° (Found : N, 16·4. $C_9H_{16}ON_2$ requires N, 16·65%). The *hydrochloride* had m. p. 200° (Found : Cl, 17·45. $C_9H_{16}ON_2,HCl$ requires Cl, 17·3%).

2-*Amino-3-phenyl-4 : 4-dimethylpyrroline N-Oxide* (X).—3-Nitro-1-phenyl-2 : 2-dimethyl-*n*-propyl cyanide (5 g.), dissolved in methyl alcohol (50 c.c.), was shaken with hydrogen and 5% palladised calcium carbonate (1 g.) until absorption of hydrogen was complete. After filtration from catalyst, the solution was evaporated on the steam-bath and the residue was treated with acetone and collected (3 g.); crystallisation from acetone–alcohol gave colourless granules, m. p. 189—190° (Found : N, 13·7. $C_{12}H_{16}ON_2$ requires N, 13·7%).

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295. *Aliphatic Nitro-compounds. Part XVI. Condensation of Hydroxymethyldialkylamines with Nitro-paraffins.*

By A. LAMBERT and J. D. ROSE.

Hydroxymethyl derivatives of secondary amines and nitromethane or nitroethane yield, on heating, only nitro-diamines of type II (R = H or Me). 1-Nitropropane gives chiefly the nitro-amine (III; R = Et) and a little nitro-diamine (I; R = Et). Nitro-amines (III; R = Me) are prepared from nitroethane and hydroxymethyldialkylamine by carrying out the

reaction for a short time at ordinary temperature. Reductions of the nitro-diamines and nitro-amines to triamines and diamines respectively are described.

In connection with other synthetic work in progress in these laboratories, amines of the types (II) and (IV) were required, and it appeared probable that the simplest and most direct method of synthesis would be from nitro-paraffins and hydroxymethyl derivatives of secondary amines, followed by hydrogenation of the nitro-amine so formed.

$$R{\cdot}CH_2{\cdot}NO_2 + 2CH_2(OH){\cdot}NR'_2 \longrightarrow \underset{\text{(I.)}}{(NR'_2{\cdot}CH_2)_3CR{\cdot}NO_2} \longrightarrow \underset{\text{(II.)}}{(NR'_2{\cdot}CH_2)_3CR{\cdot}NH_2}$$

$$R{\cdot}CH_2{\cdot}NO_2 + CH_2(OH){\cdot}NR'_2 \longrightarrow \underset{\text{(III.)}}{NR'_2{\cdot}CH_2{\cdot}CHR{\cdot}NO_2} \longrightarrow \underset{\text{(IV.)}}{NR'_2{\cdot}CH_2{\cdot}CHR{\cdot}NH_2}$$

Substances of type (I) (R = H or Me) were prepared first by Henry (*Bull. Soc. chim.*, 1896, **15**, 1225; *Ber.*, 1905, **38**, 2027) from nitromethane and nitroethane with *N*-hydroxymethylpiperidine. Despite this, de Mauney (*Bull. Soc. chim.*, 1937, **4**, 1451, 1460), as a result of experiments on the condensation of hydroxymethyl secondary amines with nitromethane, 1-nitropropane, 1-nitrobutane, and 1-nitro-octane, stated that the reaction product from primary nitro-paraffin always contained one free α-hydrogen atom, *i.e.*, nitromethane combines with two and other primary nitro-paraffins with only one mol. of hydroxymethylamine. As was shown by Zief and Mason (*J. Org. Chem.*, 1943, **8**, 1), nitroethane is an exception to this rule as it condenses with *N*-hydroxymethylpiperidine (Henry, *loc. cit.*) and with *N*-hydroxymethylmorpholine to give compounds of type (I) (R = Me). Furthermore, although 1-nitropropane reacts with *N*-hydroxymethyldiethylamine to give mainly 2-nitro-1-diethylaminobutane (III; R = R′ = Et), we have also obtained small yields of the bis-condensate, 2-*nitro*-1 : 3-*bis*(*diethylamino*)-2-*ethylpropane*, from this reaction.

The formation of amines of the type (III) (R = Me) from nitroethane is a matter of some difficulty. Attempts to degrade the bis-adducts of type (I) from nitroethane to mono-adducts of type (III) by alkaline reagents were uniformly unsuccessful, although this method is applicable to the degradation of, *e.g.*, tris(hydroxymethyl)nitromethane to 2-nitropropane-1 : 3-diol. Since 2-nitro-2-methylpropane-1 : 3-diol condenses with, *e.g.*, hydroxymethylpiperidine to give the nitro-diamine in good yield, an attempt was made to effect a similar reaction with 2-nitro-*n*-propyl alcohol. Disproportionation occurred, the only product isolated being 2-nitro-1 : 3-dipiperidino-2-methylpropane, formed by fission of the nitro-alcohol to nitroethane and formaldehyde, followed by recombination in the appropriate proportions. Similarly, 2-nitroethyl alcohol and piperidine yielded only 2-nitro-1 : 3-dipiperidinopropane, and 2-nitro*iso*propyl alcohol (from nitromethane and acetaldehyde), on treatment with hydroxymethylpiperidine, gave acetaldehyde and 2-nitro-1 : 3-dipiperidinopropane.

Finally, the nitro-monoamines of type (III) were obtained by allowing equimolecular proportions of the nitro-paraffin and the hydroxymethylamine to interact at room temperature. In this way, 2-*nitro*-1-*diethylaminopropane* was obtained in 70% yield from nitroethane and hydroxymethyldiethylamine, and 2-nitro-1-piperidinopropane was formed from nitroethane and hydroxymethylpiperidine. Although the nitro-amines were unstable and could not be obtained pure, and precipitated nitro-diamine on storage, reduction of the freshly prepared crude products gave the diamines (IV).

Experimental.

Analyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

2-*Nitro*-1 : 3-*dipiperidino*-2-*methylpropane*.—(*a*) This was prepared from hydroxymethylpiperidine and nitroethane according to Henry (*loc. cit.*); white needles from alcohol, m. p. 102°. Henry (*loc. cit.*) gives m. p. 98—99° (Found: C, 62·3; H, 9·7; N, 15·3. Calc. for $C_{14}H_{27}O_2N_3$: C, 62·8; H, 10·0; N, 15·6%).

(*b*) A mixture of 2-nitro-2-methylpropane-1 : 3-diol (Vanderbilt and Hass, *Ind. Eng. Chem.*, 1940, **32**, 34; 136 g.) and piperidine (170 g.) in alcohol (300 c.c.) was refluxed for 3 hours. After cooling, the crystals were collected, washed with a little alcohol, and dried, and had m. p. 102° alone and in admixture with a sample prepared as (*a*) above. Yield, 172 g.

2-*Nitro*-1 : 3-*bis*(*diethylamino*)-2-*methylpropane*.—Formaldehyde (40%; 75 c.c.) was treated with diethylamine (74 g.) in water (75 c.c.) at 0°, and to the mixture nitroethane (37 g.) was added with stirring at room temperature. After 16 hours' stirring the supernatant oil was isolated with ether, dried (K_2CO_3), and fractionated to give 2-*nitro*-1 : 3-*bis*(*diethylamino*)-2-*methylpropane* as an almost colourless liquid, b. p. 94—96°/0·2 mm. (Found: C, 58·8; H, 10·7; N, 16·6. $C_{12}H_{27}O_2N_3$ requires C, 58·8; H, 11·0; N, 17·1%). This diamine was unchanged by treatment with 1 mol. of sodium methoxide in methyl alcohol at room temperature. Catalytic hydrogenation with Raney nickel and hydrogen caused decomposition to low boiling products among which bis(diethylamino)methane was recognised.

2-Amino-1 : 3-bis(diethylamino)-2-methylpropane.—Crude 2-nitro-1 : 3-bis(diethylamino)-2-methylpropane, prepared as above (not distilled; total product after concentration of ethereal solution) from nitroethane (37 g.), was added dropwise with stirring to an ice-cold solution of stannous chloride (327 g.) in concentrated hydrochloric acid (500 c.c.). After 1 hours' stirring, excess of 30% aqueous sodium hydroxide was added and the product isolated with ether, dried (K_2CO_3), and fractionated. The fraction, b. p. 63—67°/0·2 mm., was dried over sodium and redistilled, giving the *amine* as a colourless oil, b. p. 60°/0·1 mm. (Found: N, 19·6. $C_{13}H_{29}N_3$ requires N, 19·5%).

2-Amino-1 : 3-bis(diethylamino)-2-ethylpropane.—A solution of diethylamine (73 g.) in water (75 c.c.) was added at 0° to formaldehyde (40%; 75 c.c.) and 1-nitropropane (45 g.) then added and the mixture stirred at room temperature for 20 hours. The upper layer was isolated with ether and distilled, giving chiefly 2-nitro-1-diethylaminobutane, b. p. 70°/0·4 mm. (cf. de Mauney, *loc. cit.*), and crude *2-nitro-1 : 3-bis(diethylamino)-2-ethylpropane* (18 g.), b. p. 108°/0·2 mm., with slight decomposition (Found: N, 15·3. $C_{13}H_{29}O_2N_3$ requires N, 16·2%). This latter was reduced as described above for the lower homologue, with stannous chloride (60 g.) and hydrochloric acid (100 c.c.) at 0°, giving *2-amino-1 : 3-bis(diethylamino)-2-ethylpropane* (5 g.) as a colourless oil, b. p. 112—114°/10 mm. (Found: C, 67·7; H, 12·8; N, 17·8. $C_{13}H_{31}N_3$ requires C, 68·1; H, 13·5; N, 18·3%). The *tripicrate* formed yellow prisms from water, m. p. 162° (Found: C, 40·6; H, 4·4; N, 17·8. $C_{13}H_{31}N_3,3C_6H_3O_7N_3$ requires C, 40·6; H, 4·4; N, 18·3%).

2-Nitro-1-diethylaminopropane.—Formaldehyde (40%; 8·1 c.c.) and diethylamine (7·3 g.) in water (10 c.c.) were mixed at 0° and nitroethane (7·5 g.) was added slowly with cooling. The mixture was kept at room temperature for 4 hours, extracted with ether, and the ethereal extract dried and distilled. *2-Nitro-1-diethylaminopropane* was obtained as a pale yellow oil (11 g.), b. p. 83·5°/11 mm. (Found: C, 52·6; H, 10·1; N, 17·3. $C_7H_{16}O_2N_2$ requires C, 52·5; H, 10·0; N, 17·5%), which decomposed slowly on keeping.

2-Amino-1-diethylaminopropane.—The nitro-amine (above) was reduced in methyl-alcoholic solution with Raney nickel and hydrogen at 70 atmospheres (initial pressure) and room temperature. Fractionation of the filtered solution gave *2-amino-1-diethylaminopropane*, b. p. 148—149°/772 mm., in 47% yield [Found: equiv. (by titration), 66·9. $C_7H_{18}N_2$ requires equiv., 65].

2-Amino-1-piperidinopropane.—Formaldehyde (87%; 81 c.c.), piperidine (85 g.), water (85 c.c.), and nitroethane (75 g.) were brought into reaction as described above for the diethylamino-analogue. 2-Nitro-1-piperidinopropane was obtained as an oil (142 g.), b. p. 99—104°/7 mm. (slight decomp.), and could not be obtained analytically pure. On keeping, decomposition occurred and 2-nitro-1 : 3-dipiperidino-2-methylpropane was precipitated. Reduction of the freshly prepared material (128 g.) with Raney nickel and hydrogen at 60 atms. and 40° gave 2-amino-1-piperidinopropane as a colourless oil (54 g.), b. p. 92—93°/15 mm. (Found: equiv. by titration), 71·4. Calc. for $C_8H_{18}N_2$: equiv., 71). Wenker (*J. Amer. Chem. Soc.*, 1938, **60**, 158), who prepared this compound by amination of 2-chloro-1-piperidinopropane, gives b. p. 193—194°/760 mm.).

Reaction of 2-Nitroethyl Alcohol with Piperidine.—2-Nitroethyl alcohol (10 g.), piperidine (20 c.c.), and dioxan (20 c.c.) were refluxed for 20 minutes and poured into water. The product was mainly 2-nitro-1 : 3-dipiperidinopropane, m. p. 93—94°, undepressed by admixture with an authentic specimen prepared from nitromethane and hydroxymethylpiperidine (Henry, *loc. cit.*).

Reaction of 2-Nitro-n-propyl Alcohol with Piperidine.—2-Nitro-*n*-propyl alcohol (21 g.) and piperidine (17 g.) were mixed; there was considerable heat evolution and the mixture was warmed on the steam-bath for one hour. On cooling, the dark liquor deposited crystals, which were collected and recrystallised from alcohol, giving 2-nitro-1 : 3-dipiperidino-2-methylpropane, m. p. 104° alone and in admixture with an authentic specimen.

Reaction of 2-Nitroisopropyl Alcohol with Piperidine and Formaldehyde.—2-Nitro*iso*propyl alcohol (10·5 g.) and piperidine (17·0 g.) were mixed and cooled, and formaldehyde (15 c.c.) was added. A pronounced smell of acetaldehyde became apparent and a crystalline solid separated. Recrystallised from alcohol, this gave 2-nitro-1 : 3-dipiperidinopropane, m. p. 93—94° alone and in admixture with an authentic specimen.

2 : 2′-Dipiperidinoisopropylamine.—2-Nitro-1 : 3-dipiperidinopropane (200 g.) in methyl alcohol (750 c.c.) was reduced with Raney nickel and hydrogen at 130 atms. (initial pressure) and 50°. Distillation of the filtered solution yielded *2 : 2′-dipiperidinoisopropylamine*, b. p. 152—154°/11 mm. Yield, 124 g. (70%) (Found: C, 68·6; H, 11·9; N, 18·4. $C_{13}H_{27}N_3$ requires C, 69·3; H, 12·0; N, 18·6%). The *trihydrochloride* formed pearly plates from aqueous alcohol, m. p. 260° (Found: Cl, 31·7. $C_{13}H_{27}N_3,3HCl$ requires Cl, 31·8%).

2 : 2′-Dipiperidinoisopropylurea.—The amine (8 g.), suspended in boiling water (100 c.c.), was treated cautiously with nitrourea; 11 g. (3 mols.) were necessary to give a clear solution. The filtered solution was treated with an excess of 10N-sodium hydroxide; the precipitated oil solidified immediately and was recrystallised from acetone. The *urea* had m. p. 86° (Found: C, 62·3; H, 10·3. $C_{14}H_{28}ON_4$ requires C, 62·6; H, 10·4%). The *dimethiodide*, from aqueous alcohol, had m. p. 257° (decomp.) (Found: N, 9·6; I, 45·7. $C_{16}H_{34}ON_4I_2$ requires N, 10·1; I, 46·0%).

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296. *Aliphatic Nitro-compounds. Part XVII. Reaction of Nitro-paraffins with Unsaturated Sulphones.**

By G. D. Buckley, (Mrs.) J. L. Charlish, and J. D. Rose.

Nitro-paraffins react with vinyl sulphones in the presence of alkaline catalysts to yield 3-nitroalkyl sulphones. The use of small amounts of catalyst results in the replacement of all the α-hydrogen atoms of the nitro-paraffin to give nitro-monosulphones from secondary nitro-paraffins, nitro-disulphones from primary nitro-paraffins, and nitro-trisulphones from nitromethane. The use of sufficient alkali to convert the whole of the nitro-paraffin into its salt results in the formation of mainly mononitro-sulphones from primary nitro-paraffins. 2-Halogenoethyl sulphones with an equivalent of alkali may be used in place of vinyl sulphones. Divinyl sulphone reacts in a similar manner: with secondary nitro-paraffins it gives 3 : 3′-dinitrodialkyl sulphones, but with primary nitro-paraffins the products are polymeric. Catalytic reduction of the nitro-sulphones affords the corresponding amino-sulphones, and their alkali metal salts give 3-keto-sulphones on treatment with mineral acids.

A convenient synthesis of vinyl sulphones is described.

Previous authors have described the addition of primary and secondary nitro-paraffins to αβ-unsaturated nitro-compounds (this series, Part VIII), cyanides (Bruson and Riener, *J. Amer. Chem. Soc.*, 1943, **65**, 23), and ketones and esters (Kohler, *J. Amer. Chem. Soc.*, 1916, **38**, 889; Sonn, *Ber.*, 1935, **68**, 148; Michael, *Ber.*, 1896, **29**, 1794), but no attempt to cause them to react with vinyl sulphones appears to have been recorded.

Although divinyl sulphone is a well-known compound, the simple monovinyl sulphones appear to be described only in the patent literature (B.P. 442,524, I.G.Farbenindustrie). Since the method described seemed unsuitable for use on the laboratory scale, the monovinyl sulphones were prepared by the following route based on the usual synthesis of divinyl sulphone (Alexander and McCombie, *J.*, 1931, 1913):

$$\begin{array}{l} R\cdot SNa + CH_2Cl\cdot CH_2\cdot OH \longrightarrow R\cdot S\cdot CH_2\cdot CH_2\cdot OH \xrightarrow{HCl} R\cdot S\cdot CH_2\cdot CH_2Cl \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow H_2O_2 \\ R\cdot SO_2\cdot CH{=}CH_2 \xleftarrow{NEt_3} R\cdot SO_2\cdot CH_2\cdot CH_2Cl \end{array}$$

This method gave *methyl*, n-*butyl*, iso*butyl*, and *p*-tolyl *vinyl sulphones* in satisfactory yield.

Nitroethane reacted readily with two molecules of *n*-butyl vinyl sulphone in presence of a small amount of potassium hydroxide to give a 75% yield of 3-*nitro*-1 : 5-*di*-(n-*butylsulphonyl*)-3-*methylpentane* (I; R = Me, R′ = Bu) which was reduced catalytically to the corresponding *amine*. In presence of one equivalent of sodium hydroxide, nitroethane reacted with one molecule of *n*-butyl vinyl sulphone to give 3-nitrodibutyl sulphone (II; R = Me) in 45% yield, together with a 13% yield of the dinitrosulphone (I; R = Me, R′ = Bu). It was not possible to suppress completely the formation of the dinitrosulphone even by the use of a large excess of alkali. 3-Nitrodibutyl sulphone was isolated as an oil by acidification of the alkaline solution with acetic or carbonic acids, but acidification with mineral acids precipitated 3-*ketodibutyl sulphone* (III; R = Me), formed by a Nef hydrolysis (*Annalen*, 1894, **280**, 263), which appears to be unusually facile in the case of γ-nitro-sulphones. The nitro-sulphone could not be purified by distillation or crystallisation, but was reduced catalytically to the easily characterised 3-aminodibutyl sulphone (*hydrochloride*).

$NO_2\cdot CR(CH_2\cdot CH_2\cdot SO_2\cdot R')_2$ (I.)

$CH_3\cdot[CH_2]_3\cdot SO_2\cdot CH_2\cdot CH_2\cdot CHR\cdot NO_2$ (II.)

$CH_3\cdot[CH_2]_3\cdot SO_2\cdot CH_2\cdot CH_2\cdot COR$ (III.)

$NO_2\cdot C(CH_2\cdot CH_2\cdot SO_2\cdot CH_3)_3$ (IV.)

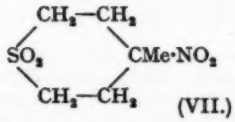
Similarly, 1-nitropropane reacted with *n*-butyl vinyl sulphone to give 3-*nitro*-1 : 5-*di*-(n-*butylsulphonyl*)-3-*ethylpentane* (I; R = Et, R′ = Bu), n-*butyl* 3-*nitroamyl sulphone* (II; R = Et), and n-*butyl* 3-*ketoamyl sulphone* (III; R = Et). Reaction of the sodium salt of *n*-butyl 3-nitroamyl sulphone with aqueous bromine gave n-*butyl* 3-*bromo*-3-*nitroamyl sulphone*. Interaction of nitromethane and methyl vinyl sulphone in presence of a little potassium hydroxide gave a 50% yield of *tris*-(2-*methylsulphonylethyl*)*nitromethane* (IV), which was reduced catalytically to *tris*-(2-*methylsulphonylethyl*)*methylamine*. *p*-Bromophenylnitromethane with methyl vinyl sulphone and a little methyltriethylammonium hydroxide gave *methyl* 3-*nitro*-3-*p*-*bromophenylpropyl sulphone* (V; R = Me) in 50% yield, and the sodium salt of

* Patent application pending.

p-bromophenylnitromethane reacted with *iso*butyl vinyl sulphone to give iso*butyl* 3-*nitro*-3-p-*bromophenylpropyl sulphone* (V; R = CH_2·$CHMe_2$) in 30% yield. 1- and 2-Nitropropane with *p*-tolyl vinyl sulphone gave respectively 3-*nitro*-1 : 5-*di*-p-*tolylsulphonyl*-3-*ethylpentane* (I; R = Et, R′ = *p*-MeC_6H_4) and 2-*nitro*-4-p-*tolylsulphonyl*-2-*methylbutane* (VI).

p-BrC_6H_4·$CH(NO_2)$·CH_2·CH_2·SO_2R
(V.)

p-MeC_6H_4·SO_2·CH_2·CH_2·CMe_2·NO_2
(VI.)


(VII.)

$[-SO_2$·CH_2·CH_2·$CMe(NO_2)$·CH_2·$CH_2-]_x$
(VIII.)

NO_2·CMe_2·CH_2·CH_2·SO_2·CH_2·CH_2·CMe_2·NO_2
(IX.)

The behaviour of divinyl sulphone was next examined. It was hoped that interaction of equimolecular proportions of nitroethane and divinyl sulphone would yield the cyclic sulphone (VII), but although a variety of conditions were tried the only products isolated were polymeric, presumably of type (VIII). The expected cyclisation is apparently hindered by steric factors. Divinyl sulphone reacted normally with two molecules of 2-nitropropane to give 3 : 3′-*dinitro*-3 : 3′-*dimethyldibutyl sulphone* (IX) which, on catalytic reduction, gave 3 : 3′-*diamino*-3 : 3′-*dimethyldibutyl sulphone*.

Experiments with 2-chloroethyl *n*-butyl sulphone showed that 2-halogenoethyl sulphones with an equivalent of sodium hydroxide could be used instead of vinyl sulphones, but the yields were lower, *e.g.*, 1-nitropropane reacted with 2-chloroethyl *n*-butyl sulphone to give 8% of 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-ethylpentane (I; R = Et, R′ = Bu) and 32% of *n*-butyl 3-nitroamyl sulphone (II; R = Et).

Experimental

Analyses are by Mr. E. S. Morton. All m. ps. are uncorrected.

Preparation of Alkyl Vinyl Sulphones.

Methyl Vinyl Sulphone.—Hydrogen peroxide (300 g. of 30%) was added dropwise to a solution of methyl 2-chloroethyl sulphide (135 g.) (*Org. Synth.*, Coll. Vol. 2, 136) in acetic acid (300 c.c.) at such a rate that the solution refluxed gently without external heating. After a further 3 hours' heating on the steam-bath, the solvents were removed by distillation under reduced pressure. The viscous residue, consisting essentially of methyl 2-chloroethyl sulphone, was added during 1 hour to a stirred solution of triethylamine (175 c.c.) in anhydrous ether (320 c.c.) and the mixture was stirred for a further 18 hours. The ethereal solution was decanted from the dark mass of triethylamine hydrochloride which was then extracted with dry acetone. The ether and acetone solutions were combined and fractionated to give *methyl vinyl sulphone* as a colourless oil (81 g.), b. p. 115—117°/19 mm. (Found : S, 29·8. $C_3H_6O_2S$ requires S, 30·2%).

n-*Butyl Vinyl Sulphone.*—2-Chloroethyl *n*-butyl sulphone was prepared by oxidation of the corresponding sulphide according to Whitner and Reid (*J. Amer. Chem. Soc.*, 1921, **43**, 637). The crude sulphone (158 g.) was added during 1 hour to a stirred solution of triethylamine (135 c.c.) in ether (250 c.c.) and the mixture was stirred for a further 18 hours. The solution was then filtered from triethylamine hydrochloride and distilled to give n-*butyl vinyl sulphone* as a colourless oil (104 g.), b. p. 135°/15 mm. (Found : S, 21·3. $C_6H_{12}O_2S$ requires S, 21·6%).

iso*Butyl Vinyl Sulphone.*—Ethylene chlorohydrin (99 g. of 30%) was added to a suspension of *iso*butylthiol (37 g.) in aqueous sodium hydroxide (115 g. of 15%) and refluxed for 1 hour. The mixture was then freed from volatile impurities by steam distillation and, after cooling, the residual oil, consisting of crude 2-hydroxyethyl *iso*butyl sulphide (40 g.), was separated, mixed with concentrated hydrochloric acid (60 c.c.) and refluxed for 4 hours. After cooling, the oily product was separated, dried ($CaCl_2$), and distilled, giving 2-*chloroethyl* iso*butyl sulphide* as a vesicant oil (39 g.), b. p. 84—85°/25 mm. (Found : Cl, 23·1. $C_6H_{13}ClS$ requires Cl, 23·3%). The chloroethyl sulphide (38 g.) was oxidised to 2-chloroethyl *iso*butyl sulphone and this was converted into the vinyl sulphone as described above for the isomer. iso*Butyl vinyl sulphone* was obtained as a colourless oil (22 g.), b. p. 132—133°/19 mm. Found : S, 21·8. $C_6H_{12}O_2S$ requires S, 21·6%).

p-*Tolyl Vinyl Sulphone.*—Hydrogen peroxide (145 g. of 30%) was added slowly to a boiling solution of *p*-tolyl 2-chloroethyl sulphide (36 g.) (Kohn and Fromm, *Ber.*, 1921, **54**, 322) in acetic acid (105 c.c.) and the mixture was refluxed for 2 hours. Water and acetic acid were removed under reduced pressure, and the residual crude *p*-tolyl 2-chloroethyl sulphone (42 g.) was dissolved in dry ether (80 c.c.) and added cautiously to a solution of triethylamine (40 c.c.) in dry ether (80 c.c.). Separation of triethylamine hydrochloride began at once, and, after standing overnight, the solution was filtered and evaporated to dryness. The residue was washed with cold water, giving a white, crystalline solid (25 g.) which, after crystallisation from alcohol, gave *p*-tolyl vinyl sulphone as white needles, m. p. 66° (I.G.Farbenindustrie, (*loc. cit.*, give m. p. 65—66°).

Reaction with Nitro-paraffins.

3-*Nitro*-1 : 5-*di*-(n-*butylsulphonyl*)-3-*methylpentane.*—Aqueous potassium hydroxide (1 c.c. of 33%) was added to a solution of nitroethane (3·5 g.) and *n*-butyl vinyl sulphone (15 g.) in alcohol (40 c.c.) and refluxed for 16 hours. After cooling, the precipitate was collected (13·25 g.) and crystallised from

alcohol, giving 3-*nitro*-1 : 5-*di*-(n-*butylsulphonyl*)-3-*methylpentane* (I; R = Me, R′ = Bu) as colourless needles, m. p. 105° (Found : N, 4·1; S, 17·1. $C_{14}H_{29}O_6NS_2$ requires N, 3·8; S, 17·25%).

3-*Nitrodibutyl Sulphone*.—Aqueous sodium hydroxide (20 c.c. of 32%) was slowly added to a stirred and ice-cooled mixture of nitroethane (15 g.) and water (80 c.c.). When a homogeneous solution had formed, *n*-butyl vinyl sulphone (30 g.) was added and the mixture stirred at 20° for 3 hours. The solid precipitate (10 g.) was collected and washed with water; it was identical with the 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-methylpentane described above. The alkaline filtrate was washed with ether to remove impurities, acidified with acetic acid (13 c.c.), and extracted with ether. The ethereal extract was dried and evaporated, leaving 3-nitrodibutyl sulphone (II; R = Me) as a pale yellow oil (21 g.) which could not be crystallised and decomposed on attempted distillation. With nitrous acid it gave a blue colouration, indicating the presence of a secondary nitro-group.

3-*Aminodibutyl Sulphone*.—Crude 3-nitrodibutyl sulphone (23 g.) in methyl alcohol (200 c.c.) was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased. The filtered solution was distilled, giving 3-aminodibutyl sulphone (8·6 g.) as a colourless, feebly basic oil, b. p. 122°/0·5 mm. The *hydrochloride* formed colourless granules, m. p. 145° (Found : Cl, 15·8. $C_8H_{19}O_2NS,HCl$ requires Cl, 15·55%). The *phenylurea* formed colourless granules from benzene, m. p. 107° (Found : N, 9·15; S, 10·1. $C_{15}H_{24}O_3N_2S$ requires N, 9·0; S, 10·25%).

3-*Ketodibutyl Sulphone* (III; R = Me).—A solution of the sodium salt of 3-nitrodibutyl sulphone, prepared from nitroethane (3·75 g.) and *n*-butyl vinyl sulphone (7·5 g.) as described above, was run into a stirred solution of sulphuric acid (6·5 c.c.) in water (30 c.c.) during 30 minutes, the temperature being kept at 10—15°. The crystalline precipitate was collected (3·8 g.) and recrystallised from a little methyl alcohol at − 20°, giving the *ketone* as colourless plates, m. p. 59° (Found : S, 16·6. $C_8H_{16}O_3S$ requires S, 16·65%). The 2 : 4-*dinitrophenylhydrazone*, m. p. 147°, formed yellow needles from alcohol (Found : N, 14·85; S, 8·6. $C_{14}H_{20}O_6N_4S$ requires N, 15·05; S, 8·6%).

3-*Amino*-1 : 5-*di*-(n-*butylsulphonyl*)-3-*methylpentane*.—3-Nitro-1 : 5-di-(*n*-butylsulphonyl)-3-methylpentane (5·8 g.) was suspended in 2-ethoxyethyl alcohol (100 c.c.) and shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption ceased; during the reaction the solid gradually passed into solution. The filtered solution was concentrated under reduced pressure and the residue crystallised from benzene, giving colourless crystals of the *amine*, m. p. 116° (Found : N, 4·1; S, 19·1. $C_{14}H_{31}O_4NS_2$ requires N, 4·15; S, 18·8%). The *acetyl* derivative formed colourless needles from water, m. p. 164° (Found : S, 16·35. $C_{16}H_{33}O_5NS_2$ requires S, 16·7%).

3-*Nitro*-1 : 5-*di*-(n-*butylsulphonyl*)-3-*ethylpentane and* n-*Butyl* 3-*Nitroamyl Sulphone*.—(a) *From* n-*butyl vinyl sulphone*. Aqueous sodium hydroxide (5 c.c. of 32%) was slowly added to a stirred and ice-cooled mixture of 1-nitropropane (4·5 g.) and water (20 c.c.). When the oil had completely dissolved, *n*-butyl vinyl sulphone (7·5 g.) was added and the mixture was stirred at 50° for 3 hours. After cooling, the solid product was collected (1·65 g.). Crystallisation from alcohol gave 3-*nitro*-1 : 5-*di*-(n-*butylsulphonyl*)-3-*ethylpentane* (I; R = Et, R′ = Bu) as colourless needles, m. p. 104° (Found : N, 3·9; S, 16·8. $C_{15}H_{31}O_6NS_2$ requires N, 3·65; S, 16·6%). The alkaline filtrate was washed with ether, acidified with acetic acid (3·5 c.c.), extracted with ether, and the dried extract concentrated, giving *n*-butyl 3-nitroamyl sulphone (II; R = Et) as a pale yellow oil (6 g.) which could not be purified by crystallisation or distillation. With nitrous acid it gave a positive test for a secondary nitro-group.

(b) *From* 2-*chloroethyl* n-*butyl sulphone*. Aqueous sodium hydroxide (12 c.c. of 32%) was added slowly to an ice-cold solution of 1-nitropropane (4·5 g.) in methyl alcohol (20 c.c.). 2-Chloroethyl *n*-butyl sulphone (9·3 g.) was then added and the mixture was stirred at 20° for 18 hours. The solution was diluted with water (50 c.c.) and the precipitate collected (1·45 g.) and recrystallised from alcohol, giving colourless needles, m. p. 104°, not depressed on admixture with 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-ethylpentane. Interaction of an aqueous solution of the sodium salt of *n*-butyl 3-nitroamyl sulphone with bromine at 10—15° gave n-*butyl* 3-*bromo*-3-*nitroamyl sulphone*, colourless crystals from alcohol, m. p. 55° (Found : S, 9·95; Br, 25·1. $C_9H_{18}O_4NBrS$ requires S, 10·1; Br, 25·3%).

n-*Butyl* 3-*Ketoamyl Sulphone* (III; R = Et).—An aqueous solution of the potassium salt of *n*-butyl 3-nitroamyl sulphone, prepared from 1-nitropropane (4·5 g.) and *n*-butyl vinyl sulphone (7·5 g.) as above, was slowly added to a stirred solution of sulphuric acid (6·5 c.c.) in water (30 c.c.) at 10—15°. Stirring was continued for 30 minutes and the precipitate (4·5 g.) was collected, washed with water, and crystallised from alcohol, giving the *ketone* as colourless needles, m. p. 89° (Found : S, 15·45. $C_9H_{18}O_3S$ requires S, 15·5%). The 2 : 4-*dinitrophenylhydrazone*, m. p. 132°, formed yellow needles from alcohol (Found : N, 14·05; S, 7·8. $C_{15}H_{22}O_6N_4S$ requires N, 14·5; S, 8·3%). The ketone was also formed by acidification of the alkaline filtrate obtained in the condensation of 1-nitropropane with 2-chloroethyl *n*-butyl sulphone (see above).

Tris-(2-*methylsulphonylethyl*)*nitromethane* (IV).—Nitromethane (6 g.), methyl vinyl sulphone (34 g.), alcohol (80 c.c.), and aqueous potassium hydroxide (1 c.c. of 33%) were refluxed for 6 hours. After cooling, the precipitate (20·6 g.) was collected, washed with alcohol, and crystallised from 2-ethoxyethyl alcohol and from acetic acid, giving colourless crystals of the *trisulphone*, m. p. 219—220° (Found : N, 3·9; S, 25·0. $C_{10}H_{21}O_8NS_3$ requires N, 3·7; S, 25·3%).

Tris-(2-*methylsulphonylethyl*)*methylamine*.—The nitro-compound (10 g.) was suspended in water (250 c.c.) and shaken with hydrogen and Raney nickel at 20°/1 atm. until absorption was complete. The mixture was then heated to the boil, filtered from catalyst, and allowed to cool. The *amine* separated in colourless needles, m. p. 218° (Found : N, 4·15; S, 27·25. $C_{10}H_{23}O_6NS_3$ requires N, 4·0; S, 27·5%).

3-*Nitro*-1 : 5-*di*-p-*tolylsulphonyl*-3-*ethylpentane* (I; R = Et, R′ = *p*-MeC_6H_4).—1-Nitropropane (3 g.), *p*-tolyl vinyl sulphone (10 g.), and aqueous potassium hydroxide (1 c.c. of 33%) in alcohol (40 c.c.) were refluxed for 16 hours, cooled, and the solid *sulphone* which separated was crystallised from acetone, giving white needles, m. p. 151° (Found : C, 55·6; H, 5·8; N, 3·25. $C_{21}H_{27}O_6NS_2$ requires C, 55·6; H, 6·0; N, 3·1%).

2-*Nitro*-4-p-*tolylsulphonyl*-2-*methylbutane* (VI).—2-Nitropropane (6 g.), *p*-tolyl vinyl sulphone (10 g.), alcohol (40 c.c.), and aqueous potassium hydroxide (1 c.c. of 33%) were refluxed for 16 hours. After cooling, the separated solid was collected and crystallised from alcohol, giving white needles of the

sulphone, m. p. 122° (Found: C, 52·95; H, 6·2; N, 4·85. $C_{12}H_{17}O_4NS$ requires C, 53·15; H, 6·25; N, 5·15%).

Methyl 3-*Nitro*-3-p-*bromophenylpropyl Sulphone* (V; R = Me).—*p*-Bromophenylnitromethane (6 g.) and methyl vinyl sulphone (8 g.) were dissolved in alcohol (40 c.c.) and a few drops of a 33% aqueous solution of methyltriethylammonium hydroxide were added. After 18 hours at 20°, the precipitate (6 g.) was collected and washed with alcohol. Recrystallisation from alcohol gave colourless needles of the *sulphone*, m. p. 142° (Found: N, 4·45; Br, 25·25; S, 10·1. $C_{10}H_{12}O_4NBrS$ requires N, 4·35; Br, 24·85; S, 9·95%).

iso*Butyl* 3-*Nitro*-3-p-*bromophenylpropyl Sulphone* (V; R = CH_2·$CHMe_2$).—*iso*Butyl vinyl sulphone (2·5 g.) was added to a solution of the sodium salt of *p*-bromophenylnitromethane (4·0 g.) in water (40 c.c.) and the mixture was stirred at 50° for 6 hours, cooled, and washed with ether. The aqueous solution was treated with acetic acid (2 c.c.), and the separated oil, which solidified on standing, was collected and washed with alcohol. The crude product (2·0 g.) was repeatedly crystallised from alcohol, giving the *sulphone* as colourless needles, m. p. 92° (Found: N, 4·3; Br, 22·2; S, 9·2. $C_{13}H_{16}O_4NBrS$ requires N, 3·85; Br, 22·0; S, 8·8%).

3 : 3′-*Dinitro*-3 : 3′-*dimethyldibutyl Sulphone* (IX).—Aqueous potassium hydroxide (1 c.c. of 33%) was added to a solution of 2-nitropropane (8·9 g.) and divinyl sulphone (5·9 g.) in alcohol (40 c.c.). The solution was refluxed for 3 hours, cooled, and the precipitate (7·85 g.) collected and recrystallised from alcohol, giving the *sulphone* as colourless leaflets, m. p. 135° (Found: N, 9·45; S, 10·55. $C_{10}H_{20}O_6N_2S$ requires N, 9·45; S, 10·85%).

3 : 3′-*Diamino*-3 : 3′-*dimethyldibutyl Sulphone*.—3 : 3′-Dinitro-3 : 3′-dimethyldibutyl sulphone (7·8 g.), suspended in 2-ethoxyethyl alcohol (100 c.c.), was shaken with Raney nickel and hydrogen at 20°/1 atm. until absorption was complete. The filtered solution was concentrated under reduced pressure, and the residue, a viscous semi-solid mass, was dissolved in water, acidified with hydrochloric acid and evaporated to dryness. After extraction with acetone, the *hydrochloride* remained as a white powder (7·2 g.), m. p. 252—255° (Found: N, 8·9; S, 10·3; Cl, 23·0. $C_{10}H_{24}O_2N_2S,2HCl$ requires N, 9·05; S, 10·35; Cl, 23·0%).

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297. *Aliphatic Nitro-compounds. Part XVIII. Interaction of Ketones and Nitro-paraffins.*

By A. LAMBERT and A. LOWE.

Interaction of acetone and nitromethane in presence of sodium methoxide, sodium hydroxide, quaternary ammonium hydroxides, or triethylamine gives chiefly nitro-*tert.*-butyl alcohol; with secondary amines as catalysts, 1 : 3-dinitro-2 : 2-dimethylpropane is the main product, and this is formed from both nitro-*tert.*-butyl alcohol and 1-nitro-2-methylprop-1-ene with nitromethane. The products obtained from other nitro-paraffins and other ketones are briefly discussed and a reaction mechanism is proposed.

THE literature on the products formed by interaction of ketones and nitro-paraffins, though not extensive, is extremely confusing. According to Fraser and Kon (*J.*, 1934, 604), condensation of acetone and some homologous ketones with nitromethane in the presence of sodium ethoxide, piperidine, pyridine, methylamine, or molecular sodium gives 1 : 3-dinitro-paraffins of the type $RR'C(CH_2·NO_2)_2$ in 15—25% yield. Nitromethane and *cyclo*hexanone with piperidine as a catalyst give 1-nitromethyl*cyclo*hexene and a little 1-nitromethyl*cyclo*hexanol, and the latter becomes the main product if sodium ethoxide is used as condensing agent. Since completion of the present work, Hass and co-workers (U.S.PP. 2,343,256; 2,383,603; cf. *Chem. Reviews*, 1943, **32**, 383; *Ind. Eng. Chem.*, 1943, **35**, 115) have described improved yields of 1 : 3-dinitro-paraffins from nitromethane and aliphatic or alicyclic ketones by using aliphatic amines as catalysts. They also report failure to duplicate Fraser and Kon's work, saying (U.S.P. 2,343,256) " this disclosure is inoperative and does not enable one skilled in the art to obtain the compounds described ".

In addition to the dinitro-paraffins, Hass also obtains from acetone and nitromethane some 1-nitro-2 : 2-dimethylpentan-4-one in yields which vary with the relative proportions of the reactants; with methyl ethyl ketone, some 1-nitro-2-ethylbut-2-ene is produced.

We have now found that, with sodium methoxide as catalyst, nitromethane and aliphatic ketones give only nitro-tertiary alcohols.

$$RR'CO + CH_3·NO_2 \longrightarrow RR'C(OH)·CH_2·NO_2$$

e.g., acetone and nitromethane gave nitro-*tert.*-butyl alcohol in 62% yield. Similar results were obtained with sodium hydroxide, quaternary ammonium hydroxides, or triethylamine as catalyst. However, by using secondary amines (diethylamine or piperidine), 68% of

1 : 3-dinitro-2 : 2-dimethylpropane was formed, but with *n*-amylamine the main product was again nitro-*tert.*-butyl alcohol.

Nitromethane and methyl ethyl ketone in the presence of piperidine have given a mixture of 1-nitro-2-methylbut-1-ene, 1-nitro-2-methylbutan-2-ol, and 2 : 2-di(nitromethyl)butane. The isolation of these compounds from one experiment, together with the formation of 1 : 3-dinitro-2 : 2-dimethylpropane from both nitro-*tert.*-butyl alcohol and 1-nitro-2-methylprop-1-ene with nitromethane, indicates that the reaction proceeds as follows :

$$RR'CO + CH_3{\cdot}NO_2 \rightleftarrows RR'C(OH){\cdot}CH_2{\cdot}NO_2 \longrightarrow RR'C{=}CH{\cdot}NO_2 \longrightarrow RR'C(CH_2{\cdot}NO_2)_2$$

Hass *et al.* (*loc. cit.*) put forward this mechanism but were unable to isolate any nitro-tertiary alcohol. It is unlikely that 1-nitro-2-diethylamino-2-methylpropane (formed from diethylamine and the nitro-olefin; see this series, Part VII) is an important intermediate product, since on reaction with nitromethane this substance gives only small yields of 1 : 3-dinitro-2 : 2-dimethylpropane.

When *cyclo*hexanone and nitromethane were brought into reaction in the presence of diethylamine, 1-nitromethyl*cyclo*hexane, 1-nitromethyl*cyclo*hexanol and a small amount of 1 : 1-di(nitromethyl)*cyclo*hexane were formed (cf. Fraser and Kon, *loc. cit.*), together with an unidentified *product*, m. p. 270—271° (*acetyl* derivative, m. p. 128—129°). The analyses of these agreed with an empirical formula, $C_{14}H_{20}O_3N_2$, but the apparent molecular weight varied with the method used for the determination.

Experimental.

Nitro-tert.-*butyl Alcohol*.—A mixture of sodium methoxide solution [from sodium (2 g.) and methyl alcohol (50 c.c.)], nitromethane (122 g.), and acetone (600 c.c.) was stirred for 3 days at 20°. After neutralisation (10N-hydrochloric acid) and filtration from salt, fractionation gave unchanged nitromethane (62 g.) and *nitro*-tert.-*butyl alcohol* (71·4 g.) as a colourless oil, b. p. 76—77°/10 mm. (Found : C, 40·7; H, 7·5; N, 11·85. $C_4H_9O_3N$ requires C, 40·3; H, 7·55; N, 11·75%). *Nitro*-tert.-*butyl acetate*, prepared from the alcohol by boiling it with acetic anhydride, is a colourless liquid, b. p. 86—88°/13 mm. (Found : N, 8·75. $C_6H_{11}O_4N$ requires N, 8·7%).

1-*Nitro*-2-*methylprop*-1-*ene*.—Nitro-*tert.*-butyl acetate (7·7 g.) was heated with sodium acetate (0·035 g.) at 110° for 30 minutes, and the mixture then distilled under reduced pressure. The distillate, b. p. 45—65°/12 mm., was diluted with ether, washed with water, dried, and fractionated, giving 1-nitro-2-methylprop-1-ene (4 g.) as a pale yellow liquid, b. p. 54—56°/11 mm. (cf. Levy and Scaife, in the press).

1 : 3-*Dinitro*-2 : 2-*dimethylpropane*.—(a) *From acetone and nitromethane*. A mixture of nitromethane (61 g.), acetone (58 g.), and diethylamine (21·5 g.) was kept at 20° for 28 days, poured into water, acidified (2N-hydrochloric acid), and extracted with chloroform. Fractionation of the dried extract gave 1 : 3-*dinitro*-2 : 2-*dimethylpropane* (55·5 g.) as an almost colourless liquid, b. p. 130—132°/10 mm., rapidly solidifying to an amorphous mass, m. p. 75—80° (Found : C, 37·2; H, 6·3; N, 17·5. $C_5H_{10}O_4N_2$ requires C, 37·0; H, 6·2; N, 17·3%).

The same substance was obtained in equal yield using piperidine in place of diethylamine; with *n*-amylamine as catalyst, only 2·5% of the dinitro-compound was formed, together with 10% of nitro-*tert.*-butyl alcohol.

(b) *From nitro*-tert.-*butyl alcohol and nitromethane*. A mixture of nitro-*tert.*-butyl alcohol (38 g.), nitromethane (20 g.), and piperidine (3 g.) was kept at 20° for 14 days. After working up in the usual way, nitro-*tert.*-butyl alcohol (2 g.) and 1 : 3-dinitro-2 : 2-dimethylpropane (19·8 g.) were obtained. Use of *n*-amylamine in place of piperidine reduced the yield of dinitro-paraffin to 8·2 g., 20 g. of the nitro-alcohol being recovered unchanged.

(c) *From nitro*-tert.-*butyl alcohol*. A mixture of nitro-*tert.*-butyl alcohol (24 g.) and diethylamine (20 g.) was kept at 20° for 6 days. After acidification (2N-hydrochloric acid), the mixture was extracted with ether and the extract fractionated, giving 1-nitro-2-methylprop-1-ene (2 g.), b. p. 54—56°/11 mm., nitro-*tert.*-butyl alcohol (3·4 g.), b. p. 75—76°/10 mm., and 1 : 3-dinitro-2 : 2-dimethylpropane (8·6 g.), b. p. 130—132°/10 mm.

(d) *From* 1-*nitro*-2-*methylprop*-1-*ene and nitromethane*. A mixture of 1-nitro-2-methylprop-1-ene (20 g.), nitromethane (12 g.), and diethylamine (3 g.), after 14 days at 20° and working up in the usual way, yielded unchanged nitro-olefin (7·8 g.) and 1 : 3-dinitro-2 : 2-dimethylpropane (6 g.), b. p. 130—132°/10 mm.

(e) *From* 1-*nitro*-2-*diethylamino*isobutane *and nitromethane*. The nitro-amine was prepared by interaction of 1-nitro-2-methylprop-1-ene (5·05 g.) and diethylamine (3·7 g.) in dry ether (15 c.c.) at 0° for 1 hour. Evaporation of the ether gave an almost completely crystalline mass of 1-nitro-2-diethylamino*iso*butane, which separated from ether on strong cooling as yellow needles, m. p. 76°. Yield, 48%. The nitro-amine decomposed rapidly on keeping and could not be analysed.

A mixture of the nitro-amine (14 g.) and nitromethane (6 g.) in ether (15 c.c.) was kept at 20° for 15 days. The yellow nitro-amine dissolved after 24 hours and the smell of diethylamine became apparent. After acidification, extraction with ether, and distillation, 1 : 3-dinitro-2 : 2-dimethylpropane (1·8 g.), b. p. 130—132°/10 mm., was obtained.

(f) *From nitro*-tert.-*butyl acetate and nitromethane*. A mixture of nitro-*tert.*-butyl acetate (14 g.), nitromethane (6 c.c.), and piperidine (2 c.c.) was kept at 20° for 16 days and worked up in the usual way. 1 : 3-Dinitro-2 : 2-dimethylpropane (5·1 g.), b. p. 134—135°/10 mm., was obtained.

1-*Nitro*-2-*methylbutan*-2-*ol*.—A mixture of nitromethane (61 g.), methyl ethyl ketone (150 c.c.), and

methyltriethylammonium hydroxide (3 c.c. of 40% aqueous solution) was kept at 20° for 5 days. The mixture was acidified (10N-hydrochloric acid) and distilled; nitromethane (45 g.) was recovered, followed by 1-*nitro*-2-*methylbutan*-2-*ol* (12 g.) as a colourless oil, b. p. 96—97°/18 mm. (Found: C, 44·8; H, 8·0; N, 10·8. $C_5H_{11}O_3N$ requires C, 45·1; H, 8·3; N, 10·5%).

1-*Nitro*-2-*methylbut*-1-*ene*.—(a) *From methyl ethyl ketone and nitromethane.* A mixture of nitromethane (100 c.c.), methyl ethyl ketone (100 c.c.), and piperidine (8 c.c.) was kept at 20° for 9 days. The solution was acidified (2N-hydrochloric acid), extracted with ether, and the extract, after being washed successively with dilute sodium hydrogen carbonate and water, was dried and fractionated, giving 1-nitro-2-methylbut-1-ene (7 g.), b. p. 62°/11 mm. (Found: C, 52·3; H, 7·55; N, 12·2. $C_5H_9O_2N$ requires C, 52·2; H, 7·8; N, 12·2%), 1-nitro-2-methylbutan-2-ol (4·4 g.), b. p. 90—91°/11 mm., and 2 : 2-di(nitromethyl)butane (11·4 g.), b. p. 92°/0·05 mm. (Fraser and Kon, *loc. cit.*, give b. p. 135—138°/9 mm.).

(b) *From* 1-*nitro*-2-*methylbutan*-2-*ol and nitromethane.* A mixture of 1-nitro-2-methylbutan-2-ol (13·3 g.), nitromethane (6·1 g.), and piperidine (3 c.c.) was kept at 20° for 14 days and worked up in the usual way. 2 : 2-Di(nitromethyl)butane (12·7 g.), b. p. 106—108°/1 mm., was obtained.

3-*Nitro*-2-*methylbutan*-2-*ol*.—A solution of sodium methoxide [from sodium (3 g.) and methyl alcohol (60 c.c.)] was mixed with nitroethane (225 g.) and acetone (935 c.c.) and the mixture stirred at 20° for 5 days. After acidification (10N-hydrochloric acid), filtration from salt and fractionation, nitroethane (170 g.) was recovered and 3-*nitro*-2-*methylbutan*-2-*ol* (51 g.) was obtained as a colourless oil, b. p. 85—86°/14 mm. (Found: C, 45·4; H, 8·0; N, 10·7. $C_5H_{11}O_3N$ requires C, 45·1; H, 8·3; N, 10·5%).

1 : 3-*Dinitro*-2 : 2-*dimethylbutane*.—A mixture of nitro-*tert.*-butyl alcohol (60 g.), nitroethane (32·5 g.) and piperidine (10 c.c.) was kept at room temperature for 3 months. After neutralisation and fractionation, 1 : 3-*dinitro*-2 : 2-*dimethylbutane* (1 g.), b. p. 128—132°/9 mm., was obtained (Found: N, 15·9. $C_6H_{12}O_4N_2$ requires N, 15·9%).

1 : 1-*Di*(*nitromethyl*)cyclo*hexane*.—(a) *From* cyclo*hexanone and nitromethane.* A mixture of *cyclo*hexanone (50 c.c.), nitromethane (30 c.c.), and diethylamine (35 c.c.) was refluxed for 10 hours. The solution was acidified (2N-hydrochloric acid) and extracted with ether. A colourless solid (12 g.) separated at this point, and was collected and crystallised from 2-ethoxyethyl alcohol, giving colourless prisms of a *substance*, m. p. 270—271° [Found: C, 63·9; H, 7·3; N, 10·8; *M* (by *X*-ray determination), 259. $C_{14}H_{20}O_8N_2$ requires C, 63·9; H, 7·2; N, 10·65%; *M*, 263]; the *acetate* had m. p. 128—129° [Found: C, 61·5; H, 6·8; N, 8·05; *M* (by *X*-ray determination), 347. $C_{18}H_{24}O_8N_2$ requires C, 62·0; H, 6·9; N, 8·05%; *M*, 348]. The constitution of this substance is unknown.

Fractionation of the ethereal solution gave 1-nitromethyl*cyclo*hexene, 1-nitromethyl*cyclo*hexanol, and 1 : 1-*di*(*nitromethyl*)cyclo*hexane* (3 g.) as a colourless oil, b. p. 105°/0·1 mm., $n_D^{20°}$ 1·4963 (Found: N, 14·2. $C_8H_{14}O_4N_2$ requires N, 13·9%).

(b) *From nitromethyl*cyclo*hexanol and nitromethane.* 1-Nitromethyl*cyclo*hexanol (30 g.; Fraser and Kon, *loc. cit.*), nitromethane (15 c.c.), and diethylamine (5 c.c.) were refluxed for 12 hours. After acidification and extraction with ether [some solid, m. p. 270—271° (1·9 g.), separated here; see above], fractionation of the dried extract afforded 1 : 1-di(nitromethyl)*cyclo*hexane, b. p. 110°/0·2 mm. (Found: N, 13·6%).

3-*Amino*-2-*methylbutan*-2-*ol*.—3-Nitro-2-methylbutan-2-ol (48 g.) in methyl alcohol (900 c.c.) was hydrogenated using Raney nickel at 20°/85 atms. (initial pressure). Fractionation of the filtered solution afforded 3-*amino*-2-*methylbutan*-2-*ol* as a colourless oil, b. p. 65—67°/17 mm. (Found: C, 58·6; H, 12·35; N, 13·9. $C_5H_{13}ON$ requires C, 58·2; H, 12·7; N, 13·6%).

1 : 3-*Diamino*-2 : 2-*dimethylpropane*.—Hydrogenation of 1 : 3-dinitro-2 : 2-dimethylpropane (25 g.) in methyl alcohol (500 c.c.) with Raney nickel (10 g.) at 20°/42 atms. (initial pressure) gave an oil, b. p. 146—156°, which on redistillation from solid potassium hydroxide yielded 1 : 3-diamino-2 : 2-dimethylpropane (11·2 g.) as a colourless oil, b. p. 154—156° (Found: C, 58·4; H, 13·6; N, 27·0. Calc. for $C_5H_{14}N_2$: C, 58·8; H, 13·7; N, 27·4%). The dihydrochloride formed prisms from alcohol, m. p. 259°; the dibenzoyl derivative, leaflets from aqueous methyl alcohol, m. p. 152° alone and in admixture with an authentic specimen prepared according to Part XII of this series.

1 : 1-*Di*(*aminomethyl*)cyclo*hexane*.—Reduction of 1 : 1-di(nitromethyl)*cyclo*hexane (5·5 g.) as described above gave 1 : 1-*di*(*aminomethyl*)cyclo*hexane* (2·6 g.) as a colourless liquid, b. p. 106—108°/10 mm. (Found: C, 67·5; H, 12·3. $C_8H_{18}N_2$ requires C, 67·6; H, 12·7%). The *dibenzoyl* derivative had m. p. 210° (Found: C, 75·3; H, 7·5; N, 8·0. $C_{22}H_{26}O_2N_2$ requires C, 75·4; H, 7·4; N, 8·0%).

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298. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part I. The Reaction of Sulphur with Mono-olefins and with* $\Delta^{1:5}$-*Diolefins.*

By E. HAROLD FARMER and F. W. SHIPLEY.

The nature of the reaction occurring at 140° between sulphur and two classes of olefins has been investigated. Olefins in general give olefin sulphides, $R{\cdot}S_x{\cdot}R'$, in which on the average half the original unsaturation is lost and x has values up to 6. In the sulphides from mono-olefins R and R' appear *on average* to be mono-olefinic and saturated respectively, except that

some redistribution appears to occur in the sulphides from hydroaromatic mono-olefins owing to the facility of occurrence of (probably secondary) dehydrogenation reactions. $\Delta^{1:5}$-Olefins give in addition to diolefin sulphides, R·S_x·R′, cyclic monosulphides which are formed from only one molecule of olefin. Thus, polyolefins displaying suitably-spaced unsaturation become both inter- and intra-molecularly cross-linked by the sulphur taken into combination. The reaction mechanism is discussed, and it is noteworthy that although substitutive and additive reactions of a radical type play an important role, additive reactions of a polar nature also participate.

THE idea has long been current that sulphur reacts with olefins in an essentially additive manner, although there is no body of evidence in the literature to relate the behaviour of sulphur as a reagent for double bonds with that of any of the numerous common additive reagents. The character of sulphur–olefin reactivity has long been a matter of interest in connexion with the mechanism of vulcanisation of rubbers and of drying oils, but the experiments and speculations of Erdmann (*Annalen*, 1908, **362**, 133), Kirchov (*Kolloid-Z.*, 1913, **13**, 49; 1914, **14**, 35), Prins (*Chem. Weekblad*, 1917, **14**, 932), and many others on this subject have done little to solve the basic problem, as it applies either to high-molecular natural and artificial rubbers or to quite simple olefins such as *iso*butylene and *cyclo*hexene. Episulphides (thioepoxides) and cyclic disulphides containing respectively the groupings (*a*) and (*b*) appear definitely never to have been obtained by the action of sulphur on olefins, and there seems to be no sound evidence to support the view that alternative structures such as (*c*) and (*d*) are formed additively at ethylenic centres.

(*a*.) (*b*.) (*c*.) (*d*.)

It is necessary, therefore, to find a new basis for formulating the course of reaction of sulphur, and in this connexion attention turns to the behaviour of the closely related element oxygen, which, also, until recently was regarded as functioning normally as a common additive reagent. Sulphur, like oxygen, contains two unpaired electrons in its outer shell, and since it shows no obvious signs in its recorded behaviour of functioning as a polar reagent it may be suspected of resembling oxygen in possessing an inherent tendency to react apolarly. Hence methods which have been successfully used in the investigation of oxygen-reactivity have been applied to the determination of the principles governing sulphur reactions. In conducting the work it has been necessary, as in the comparable oxygen studies, to divide olefins into four classes, *viz.*, (1) mono-olefins, (2) di- and poly-olefins displaying uni-spaced (*i.e.*, 1 : 4-, 1 : 4 : 7-, etc.) unsaturation, (3) di- and poly-olefins displaying bi-spaced (*i.e.*, 1 : 5-, 1 : 5 : 9-, etc., unsaturation) and (4) conjugated di- and poly-olefins, since the detailed course of reaction is greatly influenced by the unsaturation pattern.

The reaction of sulphur with olefinic materials usually becomes appreciable above 100°, and proceeds at a moderate speed at 140°, which is the most usual vulcanisation temperature for rubbers. This, the lowest temperature at which a convenient speed of reaction is obtained, was adopted for our experiments, not merely because of its common use in industrial vulcanisation processes, but also because experience soon showed that operation at substantially higher temperature is attended by serious danger of confusion arising between primary and secondary reactions. A beginning has been made by the investigation of the reaction between sulphur and *cyclo*hexene, this being of special interest, both because this reaction has twice already been examined by previous workers (Jones and Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2452; Meyer and Hohenemser, *Helv. Chim. Acta*, 1935, **18**, 1061) with results which are difficult to interpret, and because it brings into consideration whatever relationship there may be between the general or ordinary reactivity of sulphur and the possibly specialised reactivity underlying the Vesterberg procedure for the dehydrogenation of hydroaromatic compounds.

Reaction with cyclo*Hexene*.—When *cyclo*hexene is heated with sulphur for several hours in a glass tube or steel autoclave containing air, there is obtained a mixed product composed of sulphurated and unsulphurated materials. The recovered hydrocarbon is wholly unimolecular and contains only a trivial amount of *cyclo*hexadiene and benzene (<1%, determined spectroscopically as benzene), so that simple dehydrogenation of the *cyclo*hexene to a more highly unsaturated state is not an important reaction at 140° (the Vesterberg reaction is usually carried out at 200° and above), unless the *cyclo*hexadiene which is produced is subsequently used up in reaction with sulphur or hydrogen sulphide. The sulphurated products have a very large range of boiling point, but are very sensitive to elevated temperatures, even to those but little higher than the original reaction temperature, so that separation of the products by distillation must be conducted by " molecular " distillation, otherwise progressive (and hitherto unsuspected)

thermal degradation sets in, with formation of moderate yields of alkylthiol, dialkyl sulphide, and hydrogen sulphide. If the distillation temperature is kept below 150°, only the merest traces of hydrogen sulphide and thiol are formed, and the main bulk of material is easily separable with tolerable sharpness into a series of polysulphides R·S·R′, R·S_2·R′, R·S_3·R′, and R·S_4·R′. These are the invariable products of reaction under the stated conditions, but they can be progressively broken down at will by being heated for long periods at higher temperatures, and there is no doubt at all that the thiol, hydrogen sulphide, and possibly much of the monosulphide reported by the previous workers, are degradation products, and therefore only *secondary* products, of the olefin–sulphur reaction. The pentasulphide R·S_5·R′ derived from *cyclo*hexene stands at about the limit of practical distillability for non-rotary molecular stills operating at 10^{-5}—10^{-6} mm. pressure and temperatures below 150°; therefore its separation from the higher-boiling residue tended always to be very incomplete, and, in consequence, the total bulk too small to permit of its satisfactory rectification. It is perhaps significant that the undistilled residue before removal of any pentasulphide had an average composition agreeing almost exactly with that required for the hexasulphide. Variation in the proportion of sulphur employed within the observed limits of $\frac{1}{8}$ to $\frac{3}{8}$ atom of sulphur per mol. of olefin affects mainly the yield, and not the nature of the sulphides obtained.

It was at once noticeable that the alkyl radicals in these polysulphides were not wholly saturated, and, indeed, the hydrogen contents of the sulphides as determined by the most careful technique of elementary analysis available usually lay but a little above * those required for the formula C_6H_9·S_x·C_6H_{11}, or alternatively those required for an equimolecular mixture of C_6H_9·S_x·C_6H_9 and C_6H_{11}·S_x·C_6H_{11} together with (possibly) some small or large proportion of admixed C_6H_9·S_x·C_6H_{11}. In other words *the atom-ratio of hydrogen to carbon* (H/C) *in all the sulphides produced* (*in the primary reaction*) *by sulphuration was found to be identical, within the limits of analytical error, with that of the original olefin, which signified that no serious net gain or loss of hydrogen as hydrogen sulphide or thiol could have occurred to that portion of the hydrocarbon which became successfully converted into sulphides*, and hence meant that any postulation of dehydrogenation of the hydrocarbon to give hydrogen sulphide as the first necessary stage of sulphur attack must require as a corollary the complete re-addition of the hydrogen sulphide to the olefinic materials present, and must correspondingly preclude any *overall* hydrogen-enrichment of the sulphurated products at the expense of concomitantly stripped hydrocarbon molecules, but not necessarily the enrichment of individual sulphurated species (disulphides, trisulphides, etc.) at the expense of each other.

The accurate determination of total unsaturation in the partly olefinic sulphides presents a difficult practical problem which has not been satisfactorily solved: catalytic hydrogenation methods fail owing to catalyst poisoning, and all halogen addition methods which we have sought to use are invalidated owing to the high co-ordinating capacity for halogens of the combined sulphur atoms.† The determination of the distribution of unsaturation presents a still more difficult problem. At first, owing to definite analytical indications (derived from the magnitude of the hydrogen contents) that the unsaturation of the polysulphides varied appreciably within the same individual species (*i.e.*, from one sub-fraction to another), and also to the fact that a quite considerable proportion of pure saturated di*cyclo*hexyl sulphide could be isolated in the form of its methiodide from the monosulphide derived from *cyclo*hexene, it seemed likely that each species of sulphide (mono-, di-, etc.) contained some saturated material, $R_{sat.}$·S_x·$R_{sat.}$, and some dialkenyl material, $R_{|\overline{1}}$·S_x·$R_{|\overline{1}}$—these in equimolecular proportions—probably in addition to the "average compound" $R_{sat.}$·S_x·$R_{|\overline{1}}$. This generalisation is probably true in respect of the sulphuration products derived from most mono-olefins, but it does not appear to be true of the sulphurated products from hydroaromatic mono-olefins because in such examples a subsidiary phenomenon seems to enter to complicate the normal course of reaction. Infra-red spectroscopic evidence ‡ shows that much of the unsatuation surviving in the sulphides from *cyclo*hexene is conjugated unsaturation, and the most likely source of this conjugation (in view of its complete absence from the synthetically derived sulphides of all olefins and polyolefins so far examined) § is dehydrogenation, doubtless produced by secondary

* This excess doubtless merely reflects the usual tendency of hydrogen values to be rather high.

† Some progress in respect of halogen-addition methods has been made by Bloomfield (cf. *J. Soc. Chem. Ind.*, 1945, **64**, 274) since this work was carried out.

‡ We record our great indebtedness to Dr. G. B. B. M. Sutherland and Mr. N. Sheppard for their invaluable co-operation in the determination of the structure of sulphur compounds. All items of infra-red spectroscopic evidence herein depend on their observations.

§ The possibility that resonance in groups of vinyl sulphide type (·C:C·S·) is in some degree responsible has not yet been specifically examined.

reaction. There is every reason to suspect that the superior ease of dehydrogenation of *cyclo*hexene over *cyclo*hexane is due to the susceptibility of the α-methylenic hydrogen atoms to removal (as *atoms*) by the reagent, permitting the *cyclo*hexenyl radicals so formed to achieve stabilisation by disproportionation ($2C_6H_9^* \longrightarrow C_6H_8 + C_6H_{10}$), or by donation of a second hydrogen atom to sulphur or to *SH radicals; there is no obvious reason why the *cyclo*hexenyl groups of sulphides R·S_x·R′ should be immune from similar dehydrogenation, but of course to the extent that the unsaturation of some of the groups R and R′ is increased, that of others must ultimately disappear, so that the overall (or average) unsaturation is not quantitatively altered. There are no experimental indications that any considerable amount of *free* hydrogen sulphide (rather than *SH or *S_xH) is ever produced by dehydrogenation reactions and thereafter used up again in additive reactions, although minor reactivity of this type is not unlikely.

Reaction with 1-*Methyl*cyclo*hexene*.—The reaction followed exactly similar lines to that observed for *cyclo*hexene. Only a trace of free hydrogen sulphide and no thiol was formed; also the amount of monosulphide, R·S·R′, produced was very small. That portion of the product which was distillable under high vacuum below 150° consisted of mono-, di-, tetra-, and penta-sulphides, the last being distillable only with great difficulty and hence not completely isolable from the high-boiling residue, or wholly separable from admixture with the tetrasulphide. The sulphides again agreed in composition with the general formula R·S_x·R′, the groups RR′ containing between them, on average, one double bond. Probably conjugation due to dehydrogenation appears in these sulphides (although this has not been experimentally verified), so precluding them from representation by the average formula C_7H_{11}·S_x·C_7H_{13} or by the equivalent mixture of saturated and diolefinic forms C_7H_{13}·S_x·C_7H_{13} and C_7H_{11}·S_x·C_7H_{11}.

Reaction with iso*Butylene*.—In this instance also there was no appreciable amount of hydrogen sulphide or thiol produced, and the lowest sulphide isolated was R·S_2·R′. This, together with the tri- and tetra-sulphide, formed almost the whole reaction product. No conjugation of the groups R and R′ was observed in this case.

Reaction with Diolefins.—The manner of reaction of two bi-spaced olefins of the terpene group, *viz.*, dihydromyrcene, CH_3·CMe:CH·CH_2·CH_2·CMe:CH·CH_3, and geraniolene, CH_3·CMe:CH·CH_2·CH_2·CMe:CH_2 was next examined, the thermal treatment being conducted as before. With dihydromyrcene about two-thirds of the hydrocarbon was recovered in unsulphurated condition. Of the sulphurated products about half consisted of a mobile *monosulphide* $C_{10}H_{18}S$, which from its low boiling point, its not unpleasant smell, the zero value of its active hydrogen content, and the total absence of thiol reactivity, was clearly a cyclic sulphide. The remaining half was a red, viscous oil, easily decomposable, when heated above 140° or very slowly at 140° when no solvent or excess hydrocarbon was present; this product was wholly undistillable except at 10^{-5}—10^{-6} mm. in a molecular still, and apparently consisted of mixtures of sulphides of the type R·S_x·R′ analogous to these described above. The monosulphide readily formed a crystalline sulphonium iodide with methyl iodide and had a H/C ratio indistinguishable from that of the parent dihydromyrcene. The latter characteristic ruled out the possibility that hydrogen sulphide formed by dehydrogenation of some of the hydrocarbon molecules had added to the double bonds of other molecules to give a *saturated* cyclic product (*e.g.*,

$$CH_3\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH_3 + H_2S \longrightarrow CH_3\cdot \underset{\llcorner\!\!\lrcorner}{CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe\cdot CH\cdot CH_3}).$$
$$\qquad\qquad\qquad

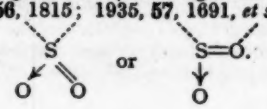
removed from a wide range of sulphur compounds by acting on them with Raney nickel containing adsorbed hydrogen; Mozingo (*J. Amer. Chem. Soc.*, **1943**, **65**, 1013) had later shown that the action in the case of typical organic sulphides consisted in the severing of the C–S bonds with formation of the corresponding simple hydrocarbons: $R{\cdot}S{\cdot}R' \xrightarrow{2H_2} RH + R'H + H_2S$.

The procedure was applied to the total sulphur product from *cyclo*hexene, 1-methyl*cyclo*hexene, and *iso*butylene, and also to homogeneous monosulphides such as di*cyclo*hexyl and di*cyclo*hexenyl sulphides. In each case there remained volatile (unimolecular) hydrocarbons free from corresponding dimeric (carbon-to-carbon cross-linked) forms.

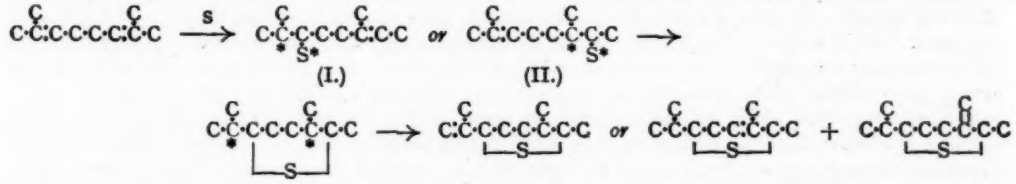
It appears, therefore, that sulphur molecules (probably chains of sulphur atoms derived by rupture of S_x rings) unite at either end with olefin molecules in virtue of the reactivity of their terminal atoms. It may tentatively be considered that such open-chained sulphur molecules will have radical ends.† In the case of the monosulphides (which are formed usually in small yield) there are two possible routes of formation: they may result from the union of single sulphur atoms (presumably $^{\bullet}S^{\bullet}$) with the olefins, or from the degradation of already formed polysulphides or polysulphide radicals, $R{\cdot}S_x{}^{\bullet}$, to give $RS^{\bullet}$. Experience has shown that when sulphur is liberated in the course of a thermal decomposition reaction (presumably in atomic condition) it is energetically reactive towards olefins, whereas elementary sulphur reacts quite slowly, even with very reactive olefins such as polyisoprenes. There is some ground, therefore, for suspecting that the small yields of monosulphides ordinarily obtained in cautiously conducted olefin–sulphur reactions may not arise from the action of monatomic sulphur. It is convenient, however, in order to simplify the argument, to assume provisionally in the following section that the reagent is monatomic biradical sulphur.

Cyclic Forms.—Owing to (1) the plurality of reaction paths open to the olefin and the sulphur reagent (having regard to the potential versatility of both), and (2) the strong possibility that cyclisation will lead to the formation of both 5- and 6- (but not 3-, 4-, and 7-) membered rings, there is little likelihood that the cyclic products formed respectively from dihydromyrcene and geraniolene will be homogeneous compounds. Efforts to separate pure or tolerably pure isomeric or structurally related forms from the two volatile sulphides—either by direct fractionation or by the formation of crystalline derivatives—proved abortive. The probability of their structural heterogeneity, however, is enhanced by the complexity of their infra-red absorption spectra in comparison with the spectra of authentic specimens of allied 6-membered saturated cyclic sulphides. The absorption curves, indeed, were in each case too complex to reveal directly the precise character of all the compounds, and for the present, necessary comparisons with corresponding 5-membered forms have had to be omitted owing to difficulties attending synthesis of the latter. But although complete interpretation of the data has not yet been possible, the deductions which have been made from a partial analysis (*q.v.*) are illuminating.

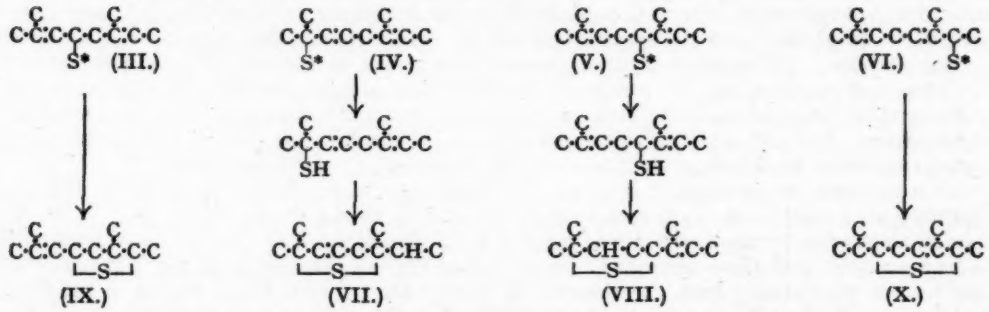
It is necessary to envisage that a radical reagent may in general attack an olefin either by replacing an α-methylenic hydrogen atom or by adding to the double bond, and it is not *a priori* impossible for the two types of reaction to occur side by side. The degree of variability to be associated with the α-methylenic (substitutive) type of reaction is mainly, but not solely (see below), that arising from the presence of two or more α-methylenic groups in the olefin undergoing attack, with the resultant possibility that attack may be initiated at more than one point in the olefinic chain. The degree of variability to be associated with the additive reaction is (for a mono-olefin) only that which could arise if the radical reagent possesses the ability to add at *either* end of the double bond. Now it has already been suggested by one of us (Farmer, *J. Soc. Chem. Ind.*, **1947**, **66**, 86) that the addition of radicals and radical reagents to unsymmetrical alkylethylenes is just as strictly and universally governed by a "radical-addition" rule as is the corresponding addition of polar reagents by the well-known "polar-addition" rule of Markovnikov. Thus, whereas Br^- would always add to the alkylated carbon atom in $CHR{:}CH_2$, $Br^{\bullet}$ (and the same applies also to other radical addenda) could just as inevitably add, if it added at all, to the other carbon atom.

† Molecular oxygen appears to have both a biradical and an unsaturated form ($\cdot\ddot{O}{:}\ddot{O}\cdot$ and $\ddot{O}{=}\ddot{O}$), the latter of which enables it to form interpolymers with some olefins. Sulphur does not appear to form interpolymers at all and hence presumably has no unsaturated reaction form, but sulphur dioxide forms interpolymers with great ease (Staudinger and Ritzenthaler, *Ber.*, **1935**, **68**, 455; Marvel *et al.*, *J. Amer. Chem. Soc.*, **1934**, **56**, 1815; **1935**, **57**, 1691, *et seq.*) and so must be able to assume a bifunctional reaction form, presumably  or .

The approach to the determination of the structures present, and to the formulation of an adequate reaction scheme, has been greatly facilitated by Naylor's parallel study of the polar and non-polar addition of hydrogen sulphide to di-isoprenic hydrocarbons (see Part II, following paper); for the results of this study are clear-cut, since not only are the cyclic products then saturated, and so free from troublesome non-uniformity in the degree and position of unsaturation, but the unsaturation pattern of the original di-isoprene is exactly that required to give either by the polar or by the non-polar process *solely* 6-membered sulphide rings. In contrast, the additive reaction which a single sulphur atom may be expected to pursue presents the high probability that marked non-homogeneity will arise in the end-product, since the bi-radical adducts (I and II) which are probably first formed, must achieve stabilisation by hydrogen transfer (*i.e.*,



probably mainly by disproportionation) in such a way that *on average* one double bond (and that bond not usually one of the original two) is retained and one lost; to some doubtless minor extent, however, the disproportionation may well yield an equimolecular mixture of the corresponding diolefinic and fully saturated sulphides.† If, however, reaction follows the α-methylenic course, attack by the reagent is likely to be confined almost entirely to the two α-methylene groups between the two double bonds, leaving those in the methyl groups intact; but owing to the capacity for resonance in any radical propene system that is formed when an α-methylenic hydrogen atom is detached (•C·C:C ⇌ C:C·C•) there will be four potential ways (III—VI) in which reaction may be initiated but only two of these, *viz.*, (III) and (VI), will lead to the successful production of cyclic forms if the radical-addition rule is to be obeyed and only 5- and 6-membered rings are capable of formation.

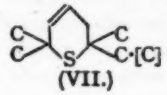


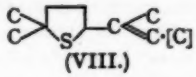
There is, however, a further possibility for the formation of cyclic sulphides which cannot be neglected, *viz.*, that which arises if the active thiol centres in (III—VI) become stabilised by capture of the hydrogen atoms (see preceding footnote) and the resulting •SH groups thereafter add themselves by polar mechanism (wherever the Markovnikov rule and the usual limitation of ring size jointly permit) to the more remote double bond. This polar type of addition would be likely to occur readily owing to the strong catalytic action of the free sulphur present (see Part II).‡ Of the four α-methylenic sulphuro-forms, however, only two, (IV) and (V), would yield cyclic sulphides (*viz.*, VII and VIII); the olefinic thiols corresponding to (III) and (VI), if formed at all, would survive. Actually, the amount of such thiol that survived as determined

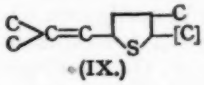
† The path taken by the disproportionation probably depends on the incidence of intra- and intermolecular hydrogen displacements respectively, the former leading exclusively to the product of average unsaturation (*i.e.*, to the mono-olefinic cyclic sulphide) and the latter probably largely to the mixture of saturated and diolefinic forms. To the extent that the addition of the sulphur to one double bond is completed (*i.e.*, the first-formed radical sulphuro-product becomes stabilised by hydrogen rejection *before* that to the other double bond occurs), to that same extent the discarded hydrogen atoms are likely to add to the •S• groups giving the thiols corresponding to (III)—(VI).

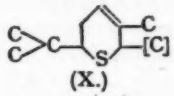
‡ Since polar and non-polar additions of hydrogen bromide (or hydrogen sulphide) to olefins occur readily side by side, there is no reason to suppose that the two kinds of addition may not occur together in this case.

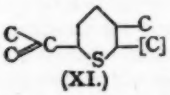
by usual methods was extremely small, but was possibly slightly underestimated; only later did the very efficient analytical and separative method used in Part II become available. Thus, altogether, the cyclic sulphides likely to be formed from dihydromyrcene by α-methylenic initiation are (VII), (VIII), (IX), and (X); and those from geraniolene precisely the same forms minus the carbo-group (CH_3) enclosed in square brackets. Correspondingly those likely to be formed by additive initiation are (X) and (XI), with possibly a very minor amount of (XII).

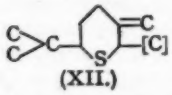

(VII.)


(VIII.)


(IX.)


(X.)


(XI.)


(XII.)

Now the infra-red absorption data show that, as regards the 6-membered forms from both dihydromyrcene and geraniolene, the skeletal pattern depicted in (VII) preponderates over that in (X); also it is plain that one or more of the isomers present contains a methyleno-grouping $CH_2{:}CRR'$ such as occurs in (XI) and in the minor isomer (XII). Hence α-methylenic initiation of the sulphuration reaction undoubtedly occurs to an important extent and may well greatly exceed additive initiation. It is of especial interest that the change from the $CRR'{:}CHR''$ structure occurring in the olefinic units of the di-isoprene to the $CHR{:}CHR'$ structure of the derived cyclic (and doubtless also of the cross-linked) sulphuro-product, as seen in (VII), with all that it implies in the way of α-methylenic initiating attack at *a* in $\cdot CH_2\cdot CMe{:}CH{-}CH_2\cdot$ as discussed above, is encountered again in the sulphuration of rubber, since Sutherland and Sheppard's infra-red spectroscopic data (private communication) show that the progress of this change keeps pace with increase in the uptake of sulphur.

It is to be noted that no products of the episulphide (thioepoxide) type have been discoverable in the fore-runs of the sulphurated mono-olefins or in the cyclic monosulphide fractions from dihydromyrcene and geraniolene; and indeed, no adequately substantiated method of obtaining such compounds save the usual one of reaction between sulphide and suitable halogeno-compounds appears yet to be known. The chemical behaviour of thioepoxy*cyclo*hexane, a typical compound of this group, differs considerably from that of the open-chain and cyclic monosulphides discussed above.

Nature of Sulphur Vulcanisation and the Stability of Sulphurated Products.—It has been shown by one of us (Farmer and Michael, *J.*, 1942, 513) that decomposing peroxides effectively promote the carbon-to-carbon cross-linking (α-methylenically initiated) of olefinic materials, and also of ketonic and carboxylated materials (cf. Farmer, " Advances in Colloid Science," 1946, II, 316). Decomposing diazo-compounds often have a similar effect, and with both classes of reagent the process follows a radical mechanism which is irreversible except in so far as the cross-linked products become broken down (and even then not usually into their exact precursors) when they are heated to the point of thermal breakdown of the weakest C–C bonds (>250°). With regard to sulphur vulcanisation, the only cross-linking which has been discoverable in the present investigation is that brought about by the linking of the hydrocarbon chains through sulphur atoms or groups of sulphur atoms. The concomitant formation of monosulphide rings in the case of di-isoprenes is to be regarded as amounting to *intra*molecular cross-linking, the different olefinic units becoming joined being in the same instead of in different molecules; such intramolecular linking is of course liable to take place wherever the reactant olefin molecules contain two or more suitably-spaced double bonds. But to the extent that cyclising sulphuration occurs at the expense of true cross-linking, the ingoing sulphur is apparently not used effectively (or at least not in the most effective way) for the conferring of " vulcanised " properties. The sulphur-vulcanisates, as a class, whether formed from short-chained olefins or high-molecular polyolefins, differ greatly from the carbon-to-carbon cross-linked vulcanisates in being highly susceptible to thermal treatment at temperatures but little above (or, possibly, where heating is very unduly prolonged, even *at*) the vulcanisation temperature. This relative instability (thermolability) appears to be a property of considerable moment in connection with the technology of natural and synthetic rubbers, causing as it does the replacement of some primary structures by secondary ones. The two structural features concerned in this instability are the C–S bonds and (in the case of *poly*sulphides) the polysulphide chains.

The Stability of C–S *Bonds.*—The susceptibility of C–S bonds to thermal degradation is

reserved for future study. In general, the strength of the bonds as it occurs in cross-linked structures is likely to vary very appreciably with the nature of the hydrocarbon chains in the immediate vicinity of the bond: indeed, having regard to the foregoing results, distinction may be made between three types of monosulphide bridge, *viz.*, (*a*) the diallylic type, C=C–C–S–C–C=C, (*b*) the alkyl-allyl type C–C–C–S–C–C=C, and (*c*) the dialkyl type, C–C–C–S–C–C–C. As regards the stability of the C–S bond to *chemical* reagents, it has previously been suggested by one of us that the well-known non-uniform action of organic bases on the sulphur vulcanisates of rubber is probably connected with differences in structure near the sulphur bridge; in the present paper, however, attention is confined to evidence concerning the breaking of C–S bonds (*a*) under the reducing action of sodium in alcohol, and (*b*) by action of methyl iodide.

Experiment showed that completely saturated sulphides such as di-*n*-propyl sulphide and di-*n*-butyl sulphide remained unattacked by the reducing agent, whereas dialkenyl sulphides such as diallyl, dicrotyl, and di*cyclo*hex-2-enyl sulphides broke down readily to give approximately equimolecular amounts of hydrogen sulphide and thiol, *e.g.*,

$$[CH_2{:}CH{\cdot}CH_2]_2S \xrightarrow{H} CH_2{:}CH{\cdot}CH_3 + CH_2{:}CH{\cdot}CH_2{\cdot}SH, \textit{ and } 2CH_2{:}CH{\cdot}CH_3 + H_2S.$$

Mixed sulphides, of which two (*propyl allyl sulphide* and cyclo*hexyl* cyclo*hexenyl* sulphide) were tested, gave an intermediate result, passing to the corresponding thiol but giving no hydrogen sulphide. Thus the C–S bond seems to be attacked by the reducing agent only when the carbon atom is in the α-position to a double bond, or in other words the sulphur atom can be reductively detached from α-methylene groups to which it is linked, but not from saturated carbon chains. The cyclic sulphides from dihydromyrcene and geraniolene gave, as would be expected from the constitutions assigned above, much thiol but no hydrogen sulphide, but reaction was considerably more sluggish, presumably on account of the alkyl substitution at each of the α-methylene groups. For comparison, a compound of the olefin thioepoxide group, *viz.*, thioepoxy*cyclo*hexane, was tested: this, in spite of the saturated chain attached on either side to the sulphur atom, underwent ready reduction to a mixture of thiol and hydrogen sulphide.

Instability of Polysulphide Chains.—The ability of sulphur atoms to become linked in chains or groups, and for elementary sulphur to exist normally in closed chains of eight, six, or possibly fewer atoms is commonly regarded as an expression of the strong co-ordinating power of sulphur, and hence there is some expectation that branching of sulphur chains due to co-ordination $\left(\textit{e.g.,}\ \begin{matrix} S{\cdot}S{\cdot}S{\cdot}S{\cdot} \\ \downarrow\ \ \downarrow \\ S\ \ S \end{matrix}\right)$ may frequently occur. The high-molecular polysulphides formed by the polymeric interaction of organic dihalides and sodium tetrasulphide (Patrick, *Trans. Faraday Soc.*, 1936, **32**, 347) are reported to contain co-ordinated sulphur atoms in their polysulphide groups, since a proportion of the sulphur can be easily removed by caustic alkali. It is reasonable to suppose that the alleged co-ordinated structure is derived directly from the tetrasulphide reagent, and that corresponding syntheses starting out from normal-chained polysulpho-reagents will yield unco-ordinated polysulphides which will not be " stripped " by caustic alkali (cf. Patrick, *loc. cit.*) or by sodium sulphite (cf. Parker, *India Rubber J.*, 1945, **108**, 387). A study of polysulphide constitution and instability will appear in a later part of this series; therefore it suffices now to point out that in our experiments the removal of sulphur by caustic alkali or sodium sulphite succeeds with the above-described products of the olefin–sulphur reaction *only* to the extent of a few units %, suggesting that the sulphur chains are almost wholly unbranched; in contrast to this, however, the diethyl tetrasulphide derived from sulphur monochloride, usually believed to be Cl·S·S·Cl, and ethylthiol ($Cl{\cdot}S_2{\cdot}Cl + 2Et{\cdot}SH \longrightarrow Et{\cdot}S{\cdot}S_2{\cdot}S{\cdot}Et + 2HCl$), as also that derived by the interaction of sodium tetrasulphide which according to the foregoing indications is branched, and ethyl iodide, surrenders nearly half its sulphur to the stripping agent. Hence there is no certainty that sulphur removed by mild stripping agents is necessarily co-ordinated sulphur, or that straight sulphur chains cannot often be ruptured and deprived of part of their sulphur by the same means.

All di- and poly-sulphides formed in the olefin–sulphur reaction decompose progressively at temperatures above 140° (especially from 160° upwards) into hydrogen sulphide, thiol, and monosulphide, but when temperatures above 140° are avoided in the working up of the products comparatively little monosulphide (with some olefins, none at all) and only traces of hydrogen sulphide are formed. Therefore the formation of a *large* proportion of monosulphide in any olefin–sulphur reaction is fairly safely to be attributed to secondary action, *i.e.*, to thermal decomposition of primary polysulphides due to too long heating or too high temperatures; apparently, however, some monosulphide is produced as a primary product, and there is no

evidence as yet to suggest that the cyclic monosulphides from the di-isoprenes are other than primary products, although thermal decomposition of polysulphides may well be able to produce additional amounts. The amount of thiol formed in the thermal decomposition of the polysulphides from *cyclo*hexene (as also those from 1-methyl*cyclo*hexene) is comparatively large, being formed apparently by progressive breaking of the S–S–S– chains, followed by capture of hydrogen atoms from surrounding olefinic molecules (R–S–S–S–S–SR′ ⟶ R–S* or R′–S* ⟶ R–SH or R′–SH). Experiment, indeed, showed that when a polysulphide mixture was distilled above the decomposition temperature, the later distillate fractions showed a H/C ratio progresively smaller and smaller until finally a solid residue containing 39·5% of sulphur but only 3·75% of hydrogen (H/C = 6 : 4·75) was left. The thiol formed by degradation appears always to be partly olefinic. Disproportionation of the sulphur content doubtless normally accompanies thiol formation when the sulphur chain is severed; Hinsberg (*Ber.*, 1910, **43**, 1874) early observed that aromatic disulphides yielded monosulphide and trisulphide as well as some thiol; and other similar instances are on record.

The Sulphur Reagent and the Initiation of Reaction.—It is provisionally concluded from the foregoing that the ordinary reaction form of sulphur in the rather slow sulphur–olefin reactions is the open, radical-terminated sulphur chain, and consequently that in the formation of the cyclic monosulphides the first step may still possibly consist in the union of one end of such sulphur chain with an olefin molecule, later to be followed by rupture of the sulphur chain (>C·S·S·S·S– ⟶ >C·S– + –S·S·S–). The preceding results provide some ground for believing that α-methylenic initiating attack by the sulphur reagent predominates over additive attack. A difficulty, however, arises in connexion with the latter view, which is left for future resolution, *viz.*, that there is a very sharp contrast between the relatively facile carbon-to-carbon molecule-linking action of peroxidic oxygen, *i.e.*, of the free radicals such as *OH derived from decomposing peroxides, ($2C_6H_{10} + 2{}^*OH \longrightarrow C_6H_9{\cdot}C_6H_9 + 2H_2O$) and the inefficient, but not unknown, similar cross-linking action of sulphur or sulphuro-radicals. This seems to suggest that the appearance of radical centres on α-methylenic carbon atoms either occurs relatively rarely in sulphur–olefin reactions or else such centres do not ordinarily get beyond the influence of the reacting sulphur.

Experimental.

(Analyses are by Dr. W. T. Chambers and Miss H. Rhodes.)

Action of Sulphur on cyclo*Hexene.*—*cyclo*Hexene (88 g.) and sulphur (25 g.) were heated together in a rotating steel autoclave for *ca.* 5 hours. A portion of the liquid product was shaken repeatedly with cold dilute potassium hydroxide solution, and the combined washings acidified with hydrochloric acid and then extracted with ether. The ethereal extract gave no appreciable residue (a smell only) of thiol on evaporation; therefore the total neutral product after being carefully freed from the unchanged *cyclo*hexene by distillation was directly fractionated. The dark brown viscous liquid was first heated at 0·1 mm. pressure (the heating bath being kept below 140°), whereupon a nearly colourless oil (4 g.), b. p. 70—100°, distilled. This was refractionated, giving (i) a monosulphide, b. p. 70° (*ca.* 0·5 g.) and (ii) a *disulphide* of b. p. 106° (*ca.* 3·4 g.). The monosulphide was a mixture of unsaturated and saturated forms (Found : C, 72·9; H, 10·5; S, 16·4; H : C = 10·2 : 6. Calc. for $C_{12}H_{20}S$: C, 73·4; H, 10·3; S, 16·35%; H : C = 10 : 6. Cal. for $C_{12}H_{22}S$: C, 76·65; H, 11·15; S, 16·2%; H : C = 11 : 6), containing some di*cyclo*hexyl sulphide since it gave with methyl iodide a poor yield of di*cyclo*hexylmethylsulphonium iodide, m. p. 110·5° (mixed m. p. with authentic specimen derived from pure di*cyclo*hexyl sulphide, 110·5°) Meyer and Hohenemser (*loc. cit.*) had shown that less cautious heating of the total sulphuration product gave a much higher yield than that here obtained of a comparable monosulphide which was thought to consist wholly or mainly of di*cyclo*hexyl sulphide, since it gave with methyl iodide the above mentioned sulphonium iodide, m. p. 110·5°. The disulphide, also, was partly unsaturated (Found : C, 63·4; H, 9·05; S, 27·5; H : C = 10·5 : 6. $C_{12}H_{20}S_2$ requires C, 63·1; H, 8·8; S, 28·05%. $C_{12}H_{22}S_2$ requires C, 62·6; H, 9·65; S, 27·8%).

The viscous residue in the still was transferred to a " molecular " still and further fractionated. In this operation a Waterman (vertical-type) still gave poor results owing to unavoidable " channeling " of the distilland on the heating surface due to low wetting-capacity for glass : hence a pot-still operating at *ca.* 10^{-5} mm. was used in preference. Numerous fractions of increasing sulphur content were successively collected, including two fractions both showing unsaturation, consisting respectively of a *tri-* and a *tetra-sulphide*. The trisulphide, $n_D^{18°}$ 1·5884, was a thick, pale yellow liquid (Found : C, 55·6; H, 7·95; S, 36·4; H : C = 10·2 : 6. $C_{12}H_{20}S_3$ requires C, 55·3; H, 7·75; S, 36·95%. $C_{12}H_{22}S_3$ requires C, 54·9; H, 8·45; S, 36·65%), and the tetrasulphide, a still more viscous yellow liquid (Found : C, 49·7; H, 6·95; S, 43·15; H : C = 10·0 : 6. $C_{12}H_{22}S_4$ requires C, 49·3; H, 6·9; S, 43·8%); the latter had $n_D^{18°}$ 1·6130, $d_4^{18°}$ 1·209, $[R_L]_D$ 84·20 (Calc. for $C_6H_{11}{\cdot}S_4{\cdot}C_6H_9$|1, using Twiss's refractivity value for the sulphur of disulphides : 85·15).

The final residue in the still (*ca.* 34 g.) was a very dark, viscous liquid, varying a little in composition from experiment to experiment. Typical analytical values were : C, 40·95; H, 5·75; S, 53·45; H : C = 10·05 : 6. (Calc. for $C_{12}H_{20}S_6$: C, 40·45; H, 5·65; S, 53·9%). The separation of a pentasulphide from this residue by further distillation could be effected only with difficulty and incompletely. One such crude product, a reddish oil, had S, 52·9% (Calc. : S, 53·9%).

The recovered *cyclo*hexene was examined spectroscopically in U.V. light, by Dr. H. P. Koch. Less than 1% of benzene and an almost negligible amount of *cyclo*hexadiene were found to be present.

Several further reactions between *cyclo*hexene and sulphur were carried out as above, diminishing proportions of sulphur being used (down to 0·18 atom per mol.). The sulphurated products were in all cases quantitatively similar to the foregoing, but the total yield diminished with reduction in the amount of sulphur employed.

Action of Sulphur on 1-*Methyl*cyclo*hexene*.—The hydrocarbon (30 g.) and sulphur (7 g.) were heated in a sealed tube at 140—145° for *ca.* 6 hrs. The unchanged hydrocarbon (15 g.) was distilled off through a column, leaving a rather thick brown liquid, from a sample of which repeated vigorous agitation with aqueous sodium hydroxide extracted no thiol. Distillation at 0·1 mm. (bath below 145°) gave only a very small amount (too small for refractionation) of crude *monosulphide*, contaminated with hydrocarbon (Found: S, 12·2. $C_{14}H_{24}S$ requires S, 14·3%). Continuation of the distillation at 10^{-5} mm. gave a succession of fractions of increasing viscosity and deepening yellow colour corresponding respectively to *disulphide* $C_7H_{11}\cdot S_2\cdot C_7H_{13}$ (Found: C, 65·0; H, 9·55; S, 25·3; H : C = 12·25 : 7. $C_{14}H_{24}S_2$ requires C, 65·6; H, 9·45; S, 25·0%), *trisulphide*, $C_7H_{11}\cdot S_3\cdot C_7H_{13}$ (Found: C, 57·85; H, 8·4; S, 34·0; H : C = 12·1 : 7. $C_{14}H_{24}S_3$ requires C, 58·25; H, 8·4; S, 33·35%), and a *tetrasulphide*, $C_7H_{11}\cdot S_4\cdot C_7H_{13}$ (Found: C, 52·25; H, 7·7; S, 39·85%; H : C = 12·3 : 7. $C_{14}H_{24}S_4$ requires C, 52·45; H, 7·55; S, 40·0%). The *pentasulphide*, which distilled with great difficulty, was not completely isolated, or wholly freed from residual tetrasulphide. The crude fraction formed a dark reddish oil (Found: C, 49·6; H, 7·5; S, 43·1. $C_{14}H_{24}S_5$ requires C, 47·6; H, 6·85; S, 43·1%).

Action of Sulphur on iso*Butylene*.—The liquid hydrocarbon (56 g.; 1 g.-mol.) was introduced at −50° into a steel autoclave which contained sulphur (35 g.; 1·1 g.-mol.). The sealed autoclave was heated at 140—150° for 14 hrs., then strongly cooled and opened. A sample of the liquid contents was tested at once for thiol by Bell and Agruss's test (*Ind. Eng. Chem. Anal.*, 1941, **13**, 297); no significant proportion was present. The unreacted *iso*butylene was allowed to evaporate, and the liquid residue (53·8 g.) distilled. The first distillate was a red liquid, b. p. 80°/12 mm. (21·8 g.), and the second a dark red rather thick liquid, b. p. 90°/0·5 mm.; there remained a dark red very viscous liquid in the still (*ca.* 14 g.). The first two distillates were separately fractionated and the products refractioned. Although these two stages of rectification did not result in perfect segregation of the individual polysulphides, an approximate separation into *di-*, *tri-*, and *tetra-sulphides* was achieved. The various fractions were yellow, reddish yellow, red and dark red liquids of increasing viscosity. The following analytical data for the fractions (*a*)—(*h*) were obtained :—

Fraction, b. p./0·5 mm.	Found, %. C.	H.	S.	*n*.	H : C.	Sulphide.
(*a*) Forerun						
(*b*) 38°	54·5	10·0	34·95	$n_D^{15°}$ 1·5005	8·75 : 4	*Di-*
(*c*) 38—39°	52·95	9·6	37·0	$n_D^{15°}$ 1·5070	8·7 : 4	
(*d*) 39—40°						
(*e*) 40—44°	—	—	44·5	$n_D^{19·5°}$ 1·5292	—	
(*f*) 44—51°	—	—	44·7	$n_D^{19·5°}$ 1·5330	—	—
(*g*) 51—60°	44·65	8·2	45·4	$n_D^{19·5°}$ 1·5407	8·8 : 4	*Tri-*
(*h*) 60—70°	43·65	7·65	47·6	$n_D^{19·5°}$ 1·5620	8·4 : 4	—
(*i*) 70—80°	—	—	—	—	—	—
(*j*) 80—90°	38·95	6·75	53·6	—	8·26 : 4	*Tetra-*
(*k*) Viscous residue	41·3	6·55	51·6	—	7·56 : 4	—

($C_8H_{16}S_2$ requires C, 54·5; H, 9·1; S, 36·35%; $C_8H_{16}S_3$ requires C, 46·1; H, 7·7; S, 46·1%; $C_8H_{16}S_4$ requires C, 40·0; H, 6·75; S, 53·3%.)

It is seen that no definite monosulphide fraction could be isolated and that the ultimate very viscous residue (although doubtless very heterogeneous, and probably containing *inter alia* some triolefinic sulphides derived by double cross-linking) approximated in average composition to tetrasulphide.

Action of Sulphur on Dihydromyrcene.—The hydrocarbon (60 g.) and sulphur (6 g.) were heated at 140° for about 5 hours in a steel rotating autoclave in an atmosphere of nitrogen. The product was a dark red, somewhat viscous liquid, from which unused hydrocarbon (*ca.* 41 g.) was distilled through a fractionating column at 15 mm. pressure (Found: C, 85·85; H, 12·95; H : C = 18·1 : 10. Calc. for $C_{10}H_{18}$: C, 86·85; H, 6·65%).

About half the remaining liquid (10 g.), which yielded no significant thiol fraction when thoroughly extracted with sodium hydroxide solution, was volatile at 15 mm. (b. p. 90—92°; $n_D^{17°}$ 1·4966). This product, a *monosulphide* of dihydromyrcene, could not be completely freed from the last traces of hydrocarbon by repeated fractionation under a good column; the sulphur content was accordingly unavoidably low (Found: C, 70·85; H, 10·7; S, 18·4; active H, 0·02. $C_{10}H_{18}S$ requires C, 70·5; H, 10·65; S, 18·85; active H, 0·0%). This monosulphide was necessarily of cyclic constitution but improbably structurally homogeneous (see p. 1523); it gave (but only in part) with methyl iodide a *methiodide*, m. p. 130° (decomp.) (Found: S, 10·0; I, 40·5. $C_{11}H_{21}SI$ requires S, 10·25; I, 40·65%).

The undistilled sulphurated residue (*ca.* 13·5 g.) was a very viscous, dark red oil, easily soluble in hydrocarbons, carbon disulphide, and ethyl alcohol. A separation of this product into two roughly equal parts was effected by extracting it with methyl alcohol. These parts, although fairly reproducible as regards elementary composition, were probably both mixtures of sulphides, since their analyses corresponded with no definite compound. The insoluble fractions obtained in successive separations were dark brown, viscous oils (Found: S, 30·2; 28·1, 28·55%), and the corresponding soluble fractions reddish-brown oils (Found: S, 25·6, 25·1, 24·6%). These materials possessed the same general characteristics as the polysulphides from the simple olefins.

Action of Sulphur on Geraniolene.—The geraniolene (b. p. 109—111°/12 mm.) was prepared from commercial citral, which was first purified by conversion into the corresponding bisulphite compound (see Hibbert and Cannon, *J. Amer. Chem. Soc.*, 1942, **46**, 119), then oxidised to geranic acid (b. p. 118—120°/0·1 mm.; $n_D^{20°}$ 1·4880) by means of silver oxide (see Bernhauer and Forster, *J. pr. Chem.*, 1936, **147**, 199), and finally decarboxylated by heating it at *ca.* 260° in a stream of nitrogen. The crude hydrocarbon, mixed with a little geranic acid, distilled during the decomposition. Several batches of hydrocarbon were united and rectified. The final product was colourless liquid, b. p. 35—36°/15 mm., $n_D^{19°}$ 1·4410.

The hydrocarbon (72 g.) was heated with sulphur (7·0 g.) in a steel rotating autoclave for 5 hrs. at 140°. The crude product yielded no thiol fraction when thoroughly extracted with sodium hydroxide solution; it contained, however, much unconsumed hydrocarbon (about ⅔ of original bulk), which was recovered by distillation.

About half the liquid residue (*ca.* 14 g.) was distillable at 12 mm. pressure, so giving a colourless, sweet-smelling liquid similar to that obtained from dihydromyrcene and sulphur. This product, $n_D^{16°}$ 1·4840, like the dihydromyrcene derivative, retained obstinately in spite of repeated refractionations traces of hydrocarbon. In consequence the sulphur content was invariably slightly low. It boiled at 65·5—66°/12 mm. (Found: C, 69·5; H, 10·5; S, 19·9; active H, 0·02. $C_9H_{16}S$ requires C, 69·2; H, 10·3; S, 20·5; active H, 0·0%).

Desulphuration of Polysulphides.—The method of desulphuration devised by Mozingo *et al.* (*loc. cit.*), employing Raney nickel powder prepared in the recommended way, was followed. The sample of nickel used evolved, on test, 116 c.c. of hydrogen per g. on being heated in butyl phthalate suspension at 220°. The sulphur compound (*ca.* 6 g.), dissolved in a little freshly-distilled *cyclo*hexane, was dropped into a layer of freshly-distilled *cyclo*hexane which acted as covering for the pyrophoric nickel (*ca.* 120 g.). Minute bubbles of gas were liberated immediately the sulphide was added. Gentle refluxing of the mixture for 3 hours completed the reaction, whereupon the solvent was removed by careful decantation, the nickel was extracted several times by boiling *cyclo*hexane, and the solvent distilled from the united *cyclo*hexane liquors through a column. The sulphides so treated were di*cyclo*hexenyl sulphide (see below), and specimens of the total sulphuration products (freed from unconsumed hydrocarbon) derived from *cyclo*hexene, 1-methylcyclohexane and *iso*butylene. In no case did any high-boiling hydrocarbon (representing a di- or poly-molecular derivative of the olefin originally sulphurated) or any sulphide remain.

Synthesis of Sulphides, Polysulphides, etc.—(1) 3 : 3′-*Di*cyclo*hexenyl sulphide.* *N*-Bromosuccinimide (73·2 g.), prepared by the method of Ziegler *et al.* (*Annalen*, 1942, **551**, 80), and *cyclo*hexene (206 c.c.) were gently refluxed for 20 mins. in pure carbon tetrachloride (300 c.c.) in the presence of a trace of benzoyl peroxide. Succinimide, which was insoluble in the tetrachloride, was gradually precipitated and was finally filtered off. The solvent was distilled off through a column and the residue fractionated. About 40 g. of almost colourless 3-bromo*cyclo*hexene, b. p. 60—61°/15 mm., $n_D^{22°}$ 1·5395, were collected (Found: C, 44·85; H, 5·7; Br, 49·3. Calc. for C_6H_9Br: C, 44·75; H, 5·65; Br, 49·6%).

3-Bromo*cyclo*hexene (12 g.), powdered sodium sulphide (5 g.), and alcohol (15 c.c.) were sealed in a Carius tube and heated to 100° for 4 hrs. The liquid in the cooled tube was filtered, diluted with ether, washed with water, dried (K_2CO_3), and the ether distilled. The residue, when distilled at *ca.* 0·1 mm. pressure gave about 4·5 g. of a colourless liquid, b. p. 81—82°, $n_D^{23°}$ 1·5506, of not unpleasant smell. This was 3 : 3′-*di*cyclo*hexenyl sulphide* (Found: C, 74·15; H, 9·45; S, 16·35. $C_{12}H_{18}S$ requires C, 74·2; H, 9·35; S, 16·35%).

(2) cyclo*Hexyl* cyclo*hexenyl sulphide.* This was formed by the action of lead *cyclo*hexyl mercaptide on 3-bromo*cyclo*hexene. *cyclo*Hexanethiol (20 g.), prepared by the hydrolysis of *cyclo*hexyl thiolacetate with alcoholic potassium hydroxide (Cunneen, *J.*, 1947, 134), was converted into its lead salt by shaking it for some hours in a stoppered vessel with excess of aqueous lead acetate. The precipitated yellow mercaptide was filtered off, well washed, dried at reduced pressure, and then suspended in alcohol (4000 c.c.). To the suspension was added 3-bromo*cyclo*hexene (29 g.), and the whole refluxed for 1 hr. on a water-bath. After filtration, most of the alcohol was distilled off through a column, and the concentrated alcoholic residue poured into water and extracted with ether. The extract was washed with water, dried ($CaCl_2$), and distilled. Much unchanged thiol passed over first, and then a colourless liquid, b. p. 69—70°/0·1 mm., $n_D^{19°}$ 1·5317, of not unpleasant smell. The latter was cyclo*hexyl* cyclo*hexenyl sulphide* (Found: C, 73·35; H, 10·2; S, 16·15. $C_{12}H_{20}S$ requires C, 73·4; H, 10·25; S, 16·3%).

(3) *Propyl allyl sulphide.* *n*-Propanethiol (45 g.) was converted into its lead salt as above, and the dried salt suspended in alcohol. To the suspension allyl bromide (70 g.) was added with shaking, and the whole refluxed for 1 hr. The resulting liquor was filtered from insoluble lead salts, poured into water, and extracted with ether. The extract was washed with water, dried ($CaCl_2$), and distilled at atmospheric pressure. The distillate (30 g.), a colourless mobile liquid, b. p. 138—140°/755 mm., was *propyl allyl sulphide* (Found: C, 61·9; H, 10·4; S, 27·7. $C_6H_{12}S$ requires C, 62·0; H, 10·4; S, 27·55%).

(4) cyclo*Hexene thioepoxide* (*episulphide*). This was obtained by the interaction of 1-chloro-2-thiocyano*cyclo*hexane and sodium sulphide ($C_6H_{10}Cl{\cdot}SCN + Na_2S \longrightarrow C_6H_{10} > S + NaCl + NaSCN$). Lead thiocyanate (235 g.) was dried, placed in a 1-l. flask, and covered with dry carbon tetrachloride (600 c.c.) to which *cyclo*hexene (49 g.) had been added. The mixture was thoroughly stirred while phenyl iododichloride (153 g.) was added in small amounts during about 45 mins., and thereafter for 1 hr. The product was then filtered from insoluble lead salts, shaken with sodium thiosulphate solution to remove free dithiocyanogen, and washed as well as possible with water (the formation of emulsions gave trouble). The carbon tetrachloride solution was dried ($CaCl_2$), filtered from polythiocyanogen, and distilled. The solvent and any iodobenzene formed in the reaction were removed at reduced pressure; the residue, consisting of 1-*chloro*-2-*thiocyano*cyclo*hexane*, distilled at 90—92°/0·1 mm. as a colourless liquid, after a forerun of 3 g. had been rejected (Found: C, 47·85; H, 5·8; N, 8·15; S, 18·3; Cl, 19·95. $C_7H_{10}NClS$ requires C, 47·85; H, 5·75; N, 8·0; S, 18·2; Cl, 20·2%); $n_D^{18·6°}$ 1·5284, $[R_L]_D$ 44·86.

The chlorothiocyano*cyclo*hexane (31 g.) was dissolved in absolute alcohol (120 c.c.), and powdered sodium sulphide (25 g.) added. The mixture, contained in a 250-c.c. flask, was thoroughly stirred and refluxed on a water-bath for 2 hours. The cooled product was poured into water and extracted several

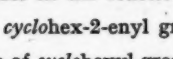
times with ether. The extract was dried (K_2CO_3), filtered, and the solvent distilled. The residue on distillation at 15 mm. pressure gave cyclo*hexene thioepoxide* as a colourless mobile oil of distinctive odour, b. p. 56—57°, $n_D^{18°}$ 1·5350 (Found: C, 63·05; H, 8·85; S, 27·95. $C_6H_{10}S$ requires C, 63·1; H, 8·8; S, 28·05%).

(5) *Diethyl tetrasulphide.* Sodium tetrasulphide (23 g.), prepared by the method of Rule and Thomas (*J.*, 1914, **105**, 177), freshly-distilled ethyl iodide (60 g.), and absolute alcohol (90 c.c.) were refluxed on a water-bath for 2 hours in a slow stream of nitrogen. The product, when cool, was poured into water, and the precipitated oil extracted with benzene. The extract was dried (K_2CO_3), and the benzene distilled off. The oily residue, on distillation at 0·1 mm., passed over mainly at 43—45°, giving an evil-smelling, yellow oil, b. p. 43—45°, $n_D^{19°}$ 1·6105. This was undoubtedly slightly impure diethyl tetrasulphide (Found: S, 67·4. Calc. for $C_4H_{10}S_4$: S, 68·8%), which Riding and Thomas (J., 1923, **123**, 3271; 1924, **125**, 2463), probably owing to the technique adopted, failed to isolate after carrying out the same reaction. A small forerun and a residue, obtained as by-products, may well have represented the corresponding di- and penta-sulphide which were reported by Riding and Thomas to be formed. Comparison of the product with that obtained by the action of sulphur monochloride on ethanethiol (cf. Chakravarti, *J.*, 1923, **123**, 966), including spectroscopic examination in U.V. light by Dr. H. P. Koch, disclosed no essential difference between the two, although the latter appears to be freer from impurities (see Part IV).

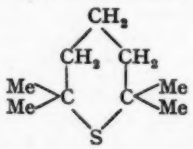
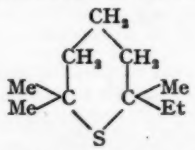
(6) The following thio-compounds required for comparison with products derived by interaction of olefins and sulphur, and for infra-red spectroscopic observations, were synthesised by methods fully described in the literature: Thiols, ethyl, *n*-butyl, and *cyclo*hexyl; sulphides, di-*n*-propyl, di-*n*-butyl, diallyl, dicrotyl; disulphides, di-*n*-butyl, dibenzyl.

Infra-red Spectra.—The following report on the characteristics of thio-compounds has been furnished by Dr. G. B. B. M. Sutherland and Mr. N. Sheppard.

(1) *The Products of the sulphur-cyclohexene reaction.* The infra-red spectra of *cyclo*hexanethiol, di*cyclo*hexyl sulphide, 3 : 3′-di*cyclo*hexenyl sulphide, and *cyclo*hexene episulphide were compared with a series of ten fractions of the reaction products.

In no case was *cyclo*hexene episulphide detectable in the reaction products, and only one of the "monosulphide" fractions showed the presence of *cyclo*hex-2-enyl groups,  . In most cases the strong bands in the spectra were nearly all those of *cyclo*hexyl groups, showing that such saturated groups predominated, but in addition every sample showed "unsaturation" bands due to C=C valency vibrations between 1590 and 1600 cm.$^{-1}$, which are in the position generally associated with unsaturation of a conjugated type. No other olefinic groups were detected.

(2) *The reaction products of sulphur with geraniolene and dihydromyrcene.* The infra-red spectra of these products were compared with those of the saturated products obtained from the reaction of the same hydrocarbons with hydrogen sulphide (Sheppard and Sutherland, this vol., p. 1540). Two general points were noticeable: (*a*) Bands at 890 cm.$^{-1}$ indicated the presence of double bonds of the type $CRR'{:}CH_2$ in the sulphur products. (*b*) There was a strong general resemblance in both cases between the spectra of the products of the reaction with sulphur and those with hydrogen sulphide. In the case of the geraniolene–sulphur product a noticeable splitting of the 1370 cm.$^{-1}$ band indicated a preponderance of *gem*-dimethyl groups (Sheppard and Sutherland, *loc. cit.*), and was further evidence for the similarity of the two products (see below). As the purification of the hydrogen sulphide products led to their identification as 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (I) and 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (II), it seems reasonable to assume that the carbon skeletons of the sulphur products

(I.)   (II.)

are closely related. On chemical grounds one would expect that the sulphur products would contain a double bond in the molecule, but our spectroscopic data are insufficient to decide this point. However, in view of the fact that the spectra of *cyclo*hexyl and *cyclo*hexenyl groups have many features in common, the spectroscopic data would be consistent with the presence of the above saturated compounds in the products *or*, alternatively, with the presence of similar compounds containing a double bond in the ring. Since $C'RR{:}CH_2$ groups are not obtainable with carbon skeletons of the above type, these bands presumably arise from another molecular species in the product.

Reductive Scission of Sulphides.—(a) *Action on saturated dialkyl sulphides.* Redistilled di-*n*-butyl sulphide (1 g.; 1 mol.) was dissolved in absolute alcohol (50 c.c.), and sodium (5 g.; 3·2 atoms) added in portions. The alcohol was kept boiling until the sodium had all dissolved, whereupon the product was cooled, poured into water, and the aqueous liquor extracted once with ether to remove traces of unchanged sulphide. The alkaline liquor was then acidified with hydrochloric acid and several times extracted with ether to remove all thiol formed in the reduction. The ethereal extract was freed from traces of mineral acid by washing it with water, and afterwards the content of thiol determined by means of silver nitrate following the procedure of Bell and Agruss (*loc. cit.*). It was found that no appreciable reduction of sulphide to thiol had occurred. The experiment was repeated with pure di-*n*-propyl sulphide, with the same result.

(b) *Action on dialkenyl sulphides.* This was examined with diallyl and di*cyclo*hexenyl sulphides. The amount of hydrogen sulphide and thiol (respectively) produced by reaction were determined from the total yield of –SH groups (including hydrogen sulphide) and the yield of thiol. These values were determined by extracting the hydrogen sulphide and thiol together from one aliquot part of the acidified (H_2SO_4), sulphide-free reduction liquor by means of benzene, and precipitating the hydrogen sulphide

from another by means of cadmium chloride, before extracting the thiol from the filtered liquor by means of ether. The details were essentially those of Bell and Agruss (*loc. cit.*). Diallyl sulphide (0·20 g.) became completely reduced, giving approximately equimolecular amounts of hydrogen sulphide (0·0260 g.) and thiol (0·062 g., calc. as allylthiol). Di*cyclo*hexenyl sulphide (0·33 g.) was similarly completely reduced, giving hydrogen sulphide (0·024 g.) and thiol (0·13 g., calc. as *cyclo*hexenthiol).

(c) *Action on alkyl alkenyl sulphides.* These sulphides gave no hydrogen sulphide on reduction, which was incomplete. *cyclo*Hexyl *cyclo*hexenyl sulphide (0·26 g.) gave thiol (doubtless *cyclo*hexyl, 0·091 g.; corresponding to *ca.* 60% reduction); propyl allyl sulphide (0·105 g.) gave thiol (doubtless propyl, 0·033 g., corresponding to *ca.* 50% reduction).

(d) *Action on cyclic sulphides.* The cyclic sulphides from dihydromyrcene and geraniolene were separately reduced in the usual way. Reduction proved to be very incomplete in each case; no hydrogen sulphide was produced but a moderate yield of alkali-soluble thiol was formed from each sulphide.

(e) *Action on thioepoxides.* This was examined only in the instance of *cyclo*hexene thioepoxide. The latter (0·148 g.) gave both hydrogen sulphide (0·010 g.) and thiol (doubtless *cyclo*hexyl, 0·08 g.).

Action of methyl iodide on monosulphides. The sulphide was in each case mixed with an equal volume of the reagent and kept in the dark overnight. A typical saturated sulphide, di*cyclo*hexyl sulphide, gave in good yield the corresponding sulphonium iodide, $SMe(C_6H_{11})_2I$, m. p. 111°. Three dialkenyl sulphides, *viz.*, diallyl, dicrotyl, and 3 : 3′-di*cyclo*hexenyl sulphide, all readily gave crystals of trimethylsulphonium iodide, m. p. 204—207° (decomp.), identical with the compound prepared by union of methyl iodide and methyl sulphide, but no stable sulphonium compound. Two alkyl alkenyl sulphides, *viz.*, *cyclo*hexyl *cyclo*hexenyl sulphide and propyl allyl sulphide, both gave non-crystallising oily products.

The monosulphide from the *cyclo*hexene–sulphur reaction gave much oily material, like the alkyl sulphides, but also a little di*cyclo*hexylmethylsulphonium iodide, m. p. 110° (mixed with authentic specimen, 110°). The cyclic sulphide from dihydromyrcene gave with methyl iodide an oil which slowly crystallised: the resulting solid (colourless prisms, m. p. 130°, from ether–alcohol) was a *methiodide* of dihydromyrcene monosulphide (Found: C, 42·0; H, 7·0; I, 40·5. $C_{11}H_{21}SI$ requires C, 42·3; H, 6·8; I, 40·65%). The cyclic sulphide from geraniolene likewise gave with methyl iodide an oil that slowly crystallised: the solid (colourless prisms, m. p. 120°, from ether–alcohol) was a *methiodide* of geraniolene monosulphide (Found: C, 39·9; H, 6·85; I, 42·25; S, 10·45. $C_{10}H_{19}SI$ requires C, 40·25; H, 6·45; I, 42·55; S, 10·75%).

*cyclo*Hexene episulphide gave with methyl iodide in a few hours much trimethylsulphonium iodide, m. p. 204—207 (Found: C, 17·55; H, 4·45. Calc. for C_3H_9SI: C, 17·7; H, 4·45%).

Removal of Polysulphide Sulphur by Chemical Reagents.—(a) *With sodium hydroxide.* The sample of sulphide was placed in a small flask (*ca.* 10 c.c.) together with 10% or 40% alkali (6 c.c.) and a few c.c. of 0·1% sodium stearate to act as wetting agent. The air space was filled with nitrogen, and the closed vessel mechanically shaken in an oil-bath adjusted to the desired temperature. After the period of treatment was completed the reaction liquor was poured into water, the oily sulphide extracted with benzene, the benzene solution washed well with water and dried (K_2CO_3), and the dry solution filtered and freed from solvent in a vacuum without heating. The decrease in sulphur content due to the action of the alkali was determined by analysis of the specimen before and after treatment in preference to determining the amount of sulphide formed in the reaction.

Typical examples of the effect of the alkali in removing sulphur are the following: The tetrasulphide from *cyclo*hexene decreased in sulphur content from 43·15 to 41·0% in 3 hrs. at 60° with 10% alkali, and from 43·15 to 40·15% in 3 hours at 80° with 40% alkali. The tetrasulphide from *cyclo*hexene decreased in sulphur content from 36·4 to 33·65% in 3 hrs. at 80° with 40% alkali. Diethyl tetrasulphide (from sodium tetrasulphide and ethyl iodide) decreased in sulphur content from 67·4 to 51·5% in 3 hrs. at 80° with sodium hydroxide, so giving nearly pure diethyl disulphide (S, 52·5%).

(b) *With sodium sulphite.* The weighed sample of sulphide (usually *ca.* 0·1 g.) was placed in 10% "AnalaR" sodium sulphite solution (100 c.c.) together with 0·1% sodium stearate (*ca.* 5 c.c.) to act as wetting agent. The solution was boiled for 2·5 hrs. during which nitrogen was slowly bubbled through. Organic matter was extracted with chloroform; then the aqueous phase was cooled at 0°, and 40% formaldehyde solution added to combine with the excess of sodium sulphite. Glacial acetic acid (10 c.c.) and 1% starch solution (3 c.c.) were next added, and the solution titrated with N/10-iodine solution to determine the yield of sodium thiosulphate and hence the amount of sulphur removed (1 mol. of $Na_2S_2O_3 \equiv 1$ atom of S). The following are typical results, losses being given in terms of total sulphur: Ethyl tetrasulphide (from sodium tetrasulphide and ethyl iodide) lost 47·5% (*i.e.*, 1·9 atoms). The polysulphide mixture (excluding cyclic monosulphide) obtained in the geraniolene–sulphur reaction lost 10·8%. The corresponding polysulphide mixture from dihydromyrcene lost 6·4%. Dibutyl tetrasulphide lost 30·1%, and *cyclo*hexene episulphide 45%.

Thermal Decomposition of Polysulphides.—Attempted distillation at *ca.* 0·1 mm. of the sulphurated products from *cyclo*hexene and 1-methyl*cyclo*hexene gave but little distillate (a little monosulphide and no thiol or hydrogen sulphide) unless the temperature of the heating bath was allowed to rise well above 140°. Prolonged heating at higher temperatures caused a slow but progressive distillation of monosulphide, thiol, and hydrogen sulphide. The tendency to decomposition of the monosulphide-free sulphurated product from *cyclo*hexene was examined at 160—170° by heating it in sealed tubes for 5 hours. The tubes were cooled in liquid air before being opened, and the main bulk of hydrogen sulphide present was allowed to evaporate slowly into lead acetate solution. The lead sulphide was filtered off, dried, and weighed. The thiol and residual hydrogen sulphide were estimated by utilising the method of Bell and Agruss (*loc. cit.*). In a typical experiment 13 g. of the sulphuration product yielded hydrogen sulphide (3·8 g.), thiol (2·5 g.), volatile sulphides (mainly monosulphide, 3·3 g.), and a small amount of non-volatile solid which was easily soluble in benzene (3·2 g.). In another experiment 5·9 g. of thio-product, after being kept at 130° and 10^{-5} mm. for 30 hrs. to ensure that no free thiol or lower sulphides were present, gave, on being heated in a sealed tube at 180—190° for 5 hrs., hydrogen sulphide (1·7 g.), thiol (1·2 g.), sulphides (mainly mono-, 1·4 g.), and a dark residue of solid (mainly crystalline) thiohydrocarbon (1·4 g.). The residue, like all residues similarly obtained by the thermal decomposition of

sulphurated *cyclo*hexene, had a much reduced H : C ratio (Found : C, 56·35; H, 3·75; S, 39·7%; H : C = 4·75/6).

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THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
WELWYN GARDEN CITY, HERTS. [*Received, January 15th*, 1947.]

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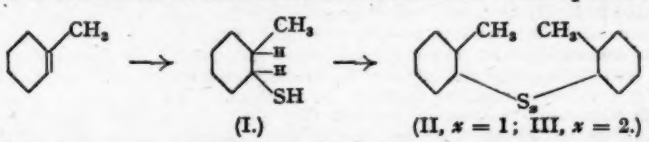
299. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part II. Mechanism of the Reaction of Hydrogen Sulphide with Mono-olefins, Di-isoprenes, and Rubber.*

By RALPH F. NAYLOR.

Hydrogen sulphide unites with mono- and di-olefins under pressure to give *normal* adducts when reaction is conducted in the presence of sulphur or a metallic sulphide as catalyst, and *abnormal* adducts when it is promoted under the influence of ultra-violet light. The adducts of both types include alkanethiols and alkyl sulphides and disulphides. The principal reaction products from the two di-isoprenes, dihydromyrcene and geraniolene, are cyclic sulphides of the tetrahydrothiopyran series, each being derived from a single molecule of the diolefin; corresponding products derived from two molecules of the diolefin are formed in much smaller yield. Rubber also gives sulphides of the latter (cross-linked) kind, formed by the linking of two or more polyolefin molecules by sulphur.

APART from the intrinsic interest of the reactivity of hydrogen sulphide with olefins, a knowledge of this reactivity is, as indicated in Part I (preceding paper), of considerable importance in the study of the reaction of sulphur with unsaturated compounds. In marked contrast to the wealth of literature on the addition of hydrogen bromide to olefins, there is very little work recorded on the corresponding reactions of hydrogen sulphide. Such accounts as are published indicate that the addition of hydrogen sulphide is difficult to effect, and that catalysts are invariably required. Among the various catalysts found to be effective are silica gel (Mailhe and Renaudie, *Compt. rend.*, **1932**, **195**, 391), nickel on kieselguhr, and certain nickel salts (Duffey, Snow, and Keyes, *Ind. Eng. Chem.*, 1934, **26**, 91; Barr and Keyes, *ibid.*, p. 1111), iron oxide and sulphide (Boëseken and Van der Linde, *Rec. Trav. chim.*, **1935**, **54**, 739), and sulphur (Jones and Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2452). The yields of addition products have seldom been high, and the direction of addition has been found in each case to follow the Markownikow rule, although a proportion of *abnormal* addition products was obtained in high-temperature heterogeneous reactions (Barr and Keyes, *loc. cit.*); this probably arose by partial isomerisation of the initial adduct. Recently, however, Vaughan and Rust (*J. Org. Chem.*, 1942, **7**, 472), by ultra-violet irradiation of mixtures of olefins and liquid hydrogen sulphide, have obtained *abnormal* adducts in a short reaction time, without the aid of the high temperatures and pressures found necessary for *normal* addition.

Since it was observed by Jones and Reid (*loc. cit.*) that the normal addition of hydrogen sulphide proceeds far less readily with *cyclo*hexene than with simple aliphatic olefins, it was not surprising to find that photo-addition of liquid hydrogen sulphide to 1-methyl*cyclo*hexene gave poor yields. As Pyrex glass, which was used for the reaction tubes, does not transmit light below 2900 A., whereas hydrogen sulphide is split into radicals only by wave-lengths of 2800 A. or less, it was necessary to add acetone as a photo-sensitiser. The products were a thiol and sulphide, and by analogy with the work of Vaughan and Rust, it may be assumed that these were 1-*methyl*cyclo*hexane*-2-*thiol* (I), and *di*-2-*methyl*cyclo*hexyl sulphide* (II). In one experiment the sulphide fraction was found to contain some disulphide (III), which although present in insufficient quantity for separation, was indicated to be present by analytical evidence. Although no previous reference has been made to the formation of disulphides in such reactions,



(I.) (II, $x = 1$; III, $x = 2$.)

it seems evident that it has arisen either by combination of two mercapto-radicals or by oxidation of the initially formed thiol.

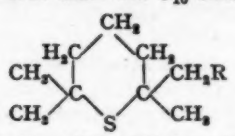
The only recorded work on the catalysis of hydrogen sulphide addition by sulphur (Jones and Reid, *loc. cit.*) suggests that the latter is one of the best catalysts for normal addition, but the relatively large quantities of catalyst then used introduce doubt as to how far the sulphur is itself reacting with the olefins and how far catalysing the addition of hydrogen sulphide. In addition, this work was conducted at 180°, at which temperature there is appreciable decomposition of some di- and poly-sulphides (see Part I; also Hinsberg, *Ber.*, 1910, **43**, 1874). It has now been confirmed that small quantities of sulphur catalyse the addition of hydrogen sulphide to *iso*butylene at *ca.* 140°; some reaction took place in absence of sulphur, but this was probably due to the catalytic effect of ferrous sulphide formed on the walls of the steel autoclave used. The reaction products were identified as being *tert.*-butyl derivatives formed by "normal" addition of the reagent to the double bond, and included di-*tert.*-butyl disulphide as well as the corresponding monosulphide and thiol. The yield of disulphide was greater than could have arisen by reaction of the sulphur catalyst with *iso*butylene, and it was still formed when the catalyst was omitted. The possibility of oxidation of the initially formed thiol was investigated by heating *tert.*-butanethiol with air in a sealed tube; no disulphide could be detected although there was some decomposition of the thiol into *tert.*-dibutyl sulphide and hydrogen sulphide. Rigorous exclusion of air from the *iso*butylene–hydrogen sulphide reaction mixture did not prevent formation of the disulphide, so the only possible mode of reaction seems to be oxidation of the thiol with concurrent reduction (hydrogenation) of the olefin, as reported by Williams and Allen (U.S.P. 2,052,268; *Chem. Abs.*, 1936, **30**, 7122) for similar hydrogen sulphide additions.

*cyclo*Hexene reacted with hydrogen sulphide in presence of a sulphur catalyst in a manner analogous to *iso*butylene, although the *cyclo*hexanethiol first produced appeared to add more readily than hydrogen sulphide to the olefin, since di*cyclo*hexyl sulphide constituted the main product. An attempt to catalyse the addition of hydrogen sulphide to 1-methyl*cyclo*hexene by ethyl dihydrogen phosphate, after the suggestion of Bähr and Corr (D.R.-P. 708,261), was unsuccessful

Sulphur-catalysed addition of hydrogen sulphide to polyisoprenes occurred more readily than it did to hydroaromatic hydrocarbons. Dihydromyrcene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe$, reacted to give a quantity of alkali-soluble material which was too small to permit of isolation of this thiol, but gave a 20% yield of an alkali-insoluble compound of formula $C_{10}H_{20}S$. Of the possible structural formulæ, (IV), (V), and (VI), assignable to this product, (VI), which is formed from (IV) or (V) by an intramolecular addition reaction, seemed the most likely in view of the insolubility of the product in alkali. Inter-molecular addition reaction yielding products containing more than one C_{10}-unit occurred

$CMe_2(SH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHR$
(IV, R = CH_3; VII, R = H.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(SH){\cdot}CH_2R$
(V, R = CH_3; VIII, R = H.)



(VI, R = CH_3; IX, R = H.)

to the extent of only 1—2%, but there appeared to be some unimolecular disulphide ($C_{10}H_{20}S_2$), which was present in insufficient quantity for isolation. Similar results were obtained by interaction of geraniolene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$, with hydrogen sulphide, the main product in this case being a thio-compound $C_9H_{18}S$, represented by (VII), VIII), or (IX). Attempts to obtain characteristic metallic salts or metallic-salt addition compounds were unsuccessful. The infra-red absorption spectrum of this thio-compound was radically different from that of the parent geraniolene, suggesting that a complete change of structure, such as is involved in the formation of a tetrahydrothiopyran ring, might have occurred. An attempt to establish this ring structure by correlation of the spectrum with that of pentamethylene sulphide was unsuccessful, as the latter exhibited an altogether different spectrum from that of the hydrogen sulphide reaction products. Synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (see this vol., p. 1106), although analytically identical with the hydrogen sulphide reaction product, showed differences in boiling point and refractive index, and had a characteristic infra-red absorption spectrum,* which could not be correlated with that of the reaction products. In particular, the latter exhibited absorption associated with unsaturated groupings of the types $CMeR{:}CH_2$ and $CRR'{:}CHR''$ and with thiol groups.

* Examination of the infra-red absorption spectra of the compounds described in this paper was carried out at Cambridge by Dr. G. B. B. M. Sutherland and Mr. N. Sheppard. The details of the spectra are discussed by these authors in the following paper.

Similar results were obtained with the dihydromyrcene–hydrogen sulphide product. The possibility of the unsaturation being due to the presence of small amounts of unchanged olefin was excluded by two experiments. Dihydromyrcene is a mixture of 2 : 6-dimethylocta-2 : 6-diene, 2 : 6-dimethylocta-2 : 6(10)-diene, and possibly 2 : 6-dimethylocta-1 : 6-diene and therefore shows absorption characteristic of $CMeR{:}CH_2$ grouping. The pure 2 : 6-isomer (which exhibits no such absorption) was prepared by sodium–ammonia reduction of geraniol (Chablay, *Ann. Chim.*, 1917, **8**, 145; Dupont, Dulou, and Desreux, *Bull. Soc. chim.*, 1939, **6**, 84) and reacted with hydrogen sulphide in the presence of sulphur. The resulting product also showed bands characteristic of $CMeR{:}CH_2$ groups, although it was established that no isomerisation of the recovered hydrocarbon had occurred. Also, examination of suitable mixtures showed that introduction of small amounts of dihydromyrcene to the synthetic thiopyran (IX) did not affect the absorption spectrum.

Substitution of aluminium sulphide for sulphur as a catalyst in the reaction of 2 : 6-dimethylocta-2 : 6-diene with hydrogen sulphide gave rise to products similar to the foregoing, but there was isolated in addition, 2 : 6-*dimercapto*-2 : 6-*dimethyloctane*, $CMe_2(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot SH$ (X). The main product, $C_{10}H_{20}S$, showed considerable difference in the absorption attributable to unsaturation from that described above, the predominant group now being $CRR'{:}CHR''$ with very little $CMeR{:}CH_2$. It is evident, therefore, that the $\cdot CMe{:}CH_2$ group arises by reaction of the sulphur itself and not of the hydrogen sulphide. That cyclic sulphides containing this group are in fact among the products of reaction of sulphur with dihydromyrcene has been indicated in Part I (*loc. cit.*).

The improbability of the occurrence in significant degree of a radical mechanism leading to "abnormal" addition in the sulphur-catalysed or metal sulphide-catalysed hydrogen sulphide reaction was indicated by demonstrating that the type of reaction obtained with 2 : 6-dimethylocta-2 : 6-diene was unaffected by the presence of quinol (polyisoprenes usually contain small quantities of peroxide which might catalyse the abnormal addition). However, the ratio of thiol to cyclic sulphides was increased.

In spite of the alkali-insolubility of the compounds $C_{10}H_{20}S$ and $C_9H_{18}S$, Zerewitinoff determinations by the micro-method of Bolland (*Trans. Inst. Rubber Ind.*, 1941, **16**, 267) indicated the presence of varying amounts of active hydrogen, presumably in the form of thiol groups * as had already been indicated by the infra-red spectra. The susceptibility of this method to traces of compounds of low molecular weight containing active hydrogen rendered it less reliable than the method recently described by Turk and Reid (*Ind. Eng. Chem. Anal.*, 1945, **17**, 713) involving titration of a solution of the thiol against a solution of cupric butyl phthalate. The presence of the thiols (IV) and (V), and (VII) and (VIII), in amounts up to 40% of the total $C_{10}H_{20}S$ and $C_9H_{18}S$ fractions was thus demonstrated. A modification of the analytical method allowed cupric butyl phthalate to be used for the qualitative removal of the thiol from the mixtures obtained by the aluminium sulphide-catalysed reactions, and this resulted in the isolation in a nearly pure state of 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (VI) and 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (IX) (see this vol., p. 1106). These two compounds exhibited absorption spectra similar to each other in the infra-red, and in both, all bands associated with unsaturation and thiol groups had disappeared. The geraniolene–hydrogen sulphide product (IX) corresponded in boiling point with the synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran and exhibited similar absorption [notably that associated with the $>CMe_2$ group which is masked in (VI) by single methyl groups] with the addition of some other absorption bands. These extra bands are almost certainly due to reaction products of small amounts of isomers of geraniolene, for, since the preparation of this involves decarboxylation of geranic acid at 270°, a partial isomerisation of the olefin is very probable. This view is confirmed by the nitrous acid test for thiols (Rheinboldt, *Ber.*, 1926, **59**, 1311; 1927, **60**, 184), which indicates that while all the dihydromyrcene products contain only tertiary thiols, those from geraniolene contain at least some primary or secondary thiols. Complete agreement was obtained between the infra-red spectrum of the cyclic sulphide from the reaction of 2 : 6-dimethylocta-2 : 6-diene and hydrogen sulphide and that of synthetic 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (see this vol., p. 1106).

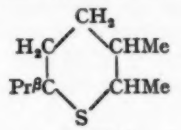
The abnormal addition of hydrogen sulphide to 2 : 6-dimethylocta-2 : 6-diene has been effected by U.V. irradiation of the reactants in the liquid phase, acetone being used as a photo-sensitiser. As in other additions, the main product was a liquid of formula $C_{10}H_{20}S$, which was shown to consist of an approximately 1 : 1 mixture of the monothiols (XI, XII) and

* It is known from earlier work that the acidity of thiols decreases progressively with increasing molecular weight (Birch and Norris, *J.*, 1925, **127**, 901).

2 : 3-*dimethyl*-6-iso*propyltetrahydrothiopyran* (XIII). Removal of the thiol by cupric butyl phthalate led to the isolation of a small quantity of the thiopyran (XIII), the absorption

$CHMe_2 \cdot CH(SH) \cdot CH_2 \cdot CH_2 \cdot CMe{:}CHMe$ (XI.)

$CMe_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot SH$ (XII.)



(XIII.)

spectrum of which exhibited a number of differences from those of the earlier products. In particular, there was some characteristic absorption which was absent in the *normal* adduct (VI), and *vice versa*. Similar differences in the absorption spectrum were exhibited by **3 : 7-*dimercapto*-2 : 6-*dimethyloctane***, $CHMe_2 \cdot CH(SH) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot SH$ (XIV), which was also isolated in small yield from the reaction product.

In addition, an intermolecularly derived ***sulphide***, $C_{20}H_{40}S_2$, formed by union of two monomercapto-units, was isolated; its analytical figures and ·SH content showed it to be a compound of the type (XV), the points of addition of the SH group, on the one hand, and of the

$$CHMe_2 \cdot CH(SH) \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot S \cdot CHPr^{\beta} \cdot CH_2 \cdot CH_2 \cdot CMe{:}CHMe \quad \text{(XV.)}$$

union through the S atom, on the other, allowing of three possible isomers (see p. 1539). This is confirmed by its infra-red absorption spectrum, which includes the characteristic absorptions of ·SH and CRR′:CHR″ groups.

Yields of the various derivatives with the olefins mentioned are indicated in Table I.

TABLE I.

Addition of hydrogen sulphide to olefins.

Olefin.	Molecular proportions (olefin = 1): H_2S.	Catalyst.	Reaction conditions: hrs.	temp.	Pressure, atm., of H_2S at working temp.	Yields of products, %. Alkali-sol. thiol.	Sulphide.	Disulphide.	Undistillable intermolecular sulphides.
*iso*Butylene	1	0·015 (S)	14	150°	45	7 [1]	4	3	0·5
,,	1	—	18	130—150	45	2 [1]	—	0·5	Negligible
,,	1	—	14	140	45	2 [1]	0·5	0·5	,,
*cyclo*Hexene	2·5	0·015 (S)	24	150	110	2·5	12	1·5	1
						Di-thiol.	$C_{10}H_{20}S$ or $C_9H_{18}S$ fraction.	Disulphide.	Intermolecular sulphides.
Dihydromyrcene	2	0·03 (S)	20	130	45	Negligible	13	2	1·5
,,	2	0·03 (S)	22	160	45	,,	18	3	2
Geraniolene	2	0·03 (S)	24	150	50	,,	14	1	1·5
,,	2	0·1 (Al_2S_3) (+ quinol)	26	150	45	[2]	10	0·1	1
2 : 6-Dimethylocta-2 : 6-diene	2	0·03 (S)	22	140—150	45	Negligible	8	[2]	[2]
,,	2	0·1 (Al_2S_3)	23	150—165	60	0·5	10	0·5	0·5
,,	2	0·1 (Al_2S_3) (+quinol)	24	150	50	[2]	8	[2]	[2]
,,	1·2	0·15 ($COMe_2$) (U.V. irradiation)	4	15	15	2	22	—	5

[1] These figures are too low as some thiol was lost on evaporation of the *iso*butylene.
[2] Not separated.

It was hoped that addition of hydrogen sulphide to rubber might be effected by shaking a rubber solution with the gas while irradiating it with ultra-violet light. However, even after 4 hours' irradiation of a solution of sol rubber (obtained by diffusion of acetone-extracted crepe rubber into light petroleum) only 1·1% of sulphur had entered the molecule. Although quartz apparatus was being used, this figure was doubled when acetone was added as a sensitiser, and small amounts of gelled material separated, which contained up to 10% of sulphur. The best value represents the saturation of 48% of the double bonds of rubber if the sulphur is assumed to be present as monosulphide.

It has been shown by Jones and Reid (*loc. cit.*) that peroxides catalyse the abnormal addition of thiols to olefins. Evidence for the catalytic effect of benzoyl peroxide on the addition of hydrogen sulphide to rubber in the present work was inconclusive. However, it was shown that

the addition reaction initiated by ultra-violet light was substantially inhibited by the natural antioxidants in rubber. Quam's report (*J. Amer. Chem. Soc.*, 1925, **47**, 103) that rubber dissolves in liquid hydrogen sulphide was confirmed with milled acetone-extracted crepe, and when the resultant solution was irradiated with ultra-violet light as before, it gave rise to a product containing 2·1% of sulphur. The addition of acetone much reduced the solubility of the rubber, but it increased the sulphur intake to 3·2%.

Solid rubber reacted with hydrogen sulphide both in the presence and in the absence of sulphur, but the latter reaction was probably catalysed by ferrous sulphide on the walls of the steel autoclave. This view was confirmed by the addition of hydrogen sulphide to rubber in the presence of ferrous sulphide and ferric oxide. Although the results obtained with dihydromyrcene and geraniolene suggest that the main reaction with polyisoprenes is intramolecular, there is always some intermolecular addition, and it may well be that this is facilitated in the case of rubber by the intermolecular entanglements of the long chains. A characteristic of all the products which have been obtained from rubber by hydrogen sulphide addition, even when the combined sulphur value is as low as 1%, is their complete insolubility in all organic solvents once they have been separated from solution. It therefore seems evident that intermolecular sulphide and disulphide links of the type observed with *cyclo*hexene and *iso*butylene are being formed. That there is a tendency for the average molecular weight to rise is shown by the fact that the observed molecular weight of a sample of milled rubber rose from 137,000 to 153,000 on treatment with hydrogen sulphide involving the incorporation of only 1% of sulphur. Rubber samples containing 2—3% of sulphur, which had been formed by reaction of solid rubber with hydrogen sulphide, exhibited many of the characteristics of a sulphur-vulcanised rubber, and although the porosity of the product precluded tensile strength tests, selected portions of the sheet were capable of over 700% elongation with good recovery. An attempt to obtain a smooth sheet for such tests by working at atmospheric pressure was unsuccessful, owing to the slowness of addition. The results obtained on both the *abnormal* and *normal* addition of hydrogen sulphide to rubber are summarised in Table II.

TABLE II.

Addition of hydrogen sulphide to rubber.

Type of rubber.	Solvent.	Sol. concn., %.	Reaction conditions: Hrs.	Light.	Catalyst or sensitiser.	S, %, in product. Fractn. remaining in solution.	Insol. fractn.
Abnormal addition.							
Sol	Benzene	1	4	u.v.	—	1·1	—
Sol	,,	1	4	,,	5% $COMe_2$	2·25	—
Sol	,,	1	4	,,	5% $COMe_2$	2·65	10·1
Sol	,,	1	4	,,	Bz_2O_2 & 5% $COMe_2$	2·1	—
Crepe	,,	1	4	,,	5% $COMe_2$	0·8	—
Milled acetone-extracted crepe	,,	9	7·5	,,	5% $COMe_2$	1·0	{4·5 2·2
,, ,,	,,	1	4	daylight (at 75°)	—	0·15	—
,, ,,	,,	1	1		Bz_2O_2	0·30	—
,, ,,	Liq. H_2S	1	0·4	u.v.	—	2·07	—
,, ,,	,,	1	0·4	,,	5% $COMe_2$	3·2	1·3
Normal addition.							
			Hrs.	Temp.	press., atm., of H_2S.		
Milled crepe	—	—	2	140°	30	—	—	{1·85 2·2
,,	—	—	2	140	30	½% S	—	{2·7 2·8
,,	—	—	2	140—160	30	—	—	2·75*
,,	—	—	2	140—160	30	½% S	—	3·25*
Milled acetone-extracted crepe	—	—	2	140—160	30	—	—	3·15*
Milled crepe	—	—	2	260	40	—	—	8·45
,,	—	—	48	140	1	—	—	0·5
,,	—	—	48	140	1	½% S	—	0·8
Milled acetone-extracted crepe	*cyclo*Hexane	8	20	85—103	20	FeS & Fe_2O_3	1·1	4·8

* After acetone extraction of the product.

Experimental.

(Microanalyses were carried out by Dr. W. T. Chambers, Miss H. Rhodes, and Miss E. Farquhar.)

Hydrogen sulphide was prepared and purified by Quam's method (*loc. cit.*).

1-*Methyl*cyclo*hexene and Hydrogen Sulphide.*—1-Methyl*cyclo*hexene (10 g.), liquid hydrogen sulphide (7 g.), and acetone (1 g.) were sealed in a Pyrex tube, and irradiated with ultra-violet light for 60 minutes at 0°. The product was extracted with 10% aqueous sodium hydroxide (50 ml.) and with ether. From the alkaline extract was obtained 1-*methyl*cyclo*hexane-2-thiol* (1 g.), which was distilled at 56°/14 mm.; it was an evil-smelling, colourless liquid, which froze when cooled to 0° (Found: C, 63·8; H, 10·8; S, 23·8. $C_7H_{14}S$ requires C, 64·6; H, 10·8; S, 24·6%). The neutral portion, which was very small, distilled at 106°/0·1 mm., and appeared to consist of a mixture of di-2-methyl*cyclo*hexyl sulphide and disulphide (Found: C, 69·8; H, 10·7; S, 18·5. Calc. for $C_{14}H_{26}S$: C, 74·3; H, 11·5; S, 14·2. Calc. for $C_{14}H_{26}S_2$: C, 65·1; H, 10·1; S, 24·8%).

iso*Butylene and Hydrogen Sulphide* (*Sulphur Catalyst*).—A mixture of *iso*butylene (56 g.), solid hydrogen sulphide (38 g.), and sulphur (0·5 g.) was introduced into a steel autoclave and heated for 14 hours at *ca.* 150°. After evaporation of unchanged hydrocarbon the product (12·2 g.) contained *tert.*-butanethiol (6·0 g.), di-*tert.*-butyl sulphide (2·6 g.), di-*tert.*-butyl disulphide (2·8 g.), and a non-volatile residue (0·5 g.). The thiol was redistilled to give a liquid, b. p. 63°, $n_D^{18°}$ 1·4212, and identified as its mercuric salt, m. p. 159—160° (Found: S, 16·8. Calc. for $C_8H_{18}S_2Hg$: S, 16·9%). After thorough extraction with 10% aqueous alkali, the monosulphide distilled at 51°/16 mm. and had $n_D^{18°}$ 1·4511 (Found: C, 65·5; H, 12·3; S, 21·9. Calc. for $C_8H_{18}S$: C, 65·7; H, 12·3; S, 21·9%). Fractionation of the disulphide gave a liquid, b. p. 79—80°/16 mm., $n_D^{17°}$ 1·4928 (Found: C, 53·9; H, 10·2; S, 35·9. Calc. for $C_8H_{18}S_2$: C, 53·9; H, 10·1; S, 35·9%).

In absence of sulphur, 14 hours' heating of a mixture of *iso*butylene (56 g.) and hydrogen sulphide (38 g.) gave a product containing *tert.*-butanethiol (1 g.), di-*tert.*-butyl sulphide (0·6 g.), and di-*tert.*-butyl disulphide (0·7 g.). In a further similar experiment, when air was completely excluded, after 18 hours at 130—150° the product consisted of thiol (1·5 g.), disulphide (0·4 g.), and a negligible quantity of sulphide.

tert.-Butanethiol (2 g.) was heated in a sealed tube in presence of air for 14 hours at 140—150°; it was mainly unchanged but contained di-*tert.*-butyl sulphide (0·2 g.) and hydrogen sulphide.

cyclo*Hexene and Hydrogen Sulphide* (*Sulphur Catalyst*).—A mixture of *cyclo*hexene (100 g.), hydrogen sulphide (100 g.), and sulphur (0·5 g.) was heated for 24 hours at *ca.* 150°. Fractional distillation of the product gave *cyclo*hexanethiol (3·5 g.), di*cyclo*hexyl sulphide (13·5 g.), di*cyclo*hexyl disulphide (2·5 g.), and a residue (1·5 g.). The thiol was purified by conversion with 10% aqueous alkali into its sodium salt, whose solution was acidified with hydrochloric acid under nitrogen; the redistilled thiol had b. p. 41°/12 mm., $n_D^{18°}$ 1·4988 (Found: C, 62·1; H, 10·2; S, 27·3. Calc. for $C_6H_{12}S$: C, 62·0; H, 10·3; S, 27·6%). To an alcoholic solution of the thiol was added hot aqueous mercuric cyanide. The precipitated oil was dissolved in hot alcohol and left to crystallise; on recrystallisation from methanol the *mercaptide* was obtained as colourless crystals, m. p. 71° (Found: S, 14·9; Hg, 46·4. $C_{12}H_{22}S_2Hg$ requires S, 14·9; Hg, 46·4%). The redistilled sulphide was a colourless liquid, b. p. 74°/0·2 mm., $n_D^{18·5°}$ 1·5162 (Found: C, 72·5; H, 11·1; S, 16·2. Calc. for $C_{12}H_{22}S$: C, 72·7; H, 11·1; S, 16·2%), and the disulphide a pale yellow liquid b. p. 110—112°/0·2 mm., $n_D^{18·5°}$ 1·5557 (Found: C, 63·0; H, 9·7; S, 27·4. Calc. for $C_{12}H_{22}S_2$: C, 62·7; H, 9·6; S, 27·8%). On standing with methyl iodide the monosulphide yielded a yellow oil which slowly solidified to the *methiodide* of di*cyclo*hexyl sulphide; recrystallisation from ether containing a little alcohol gave colourless crystals, m. p. 110—111° (Found: I, 37·4. $C_{13}H_{25}SI$ requires I, 37·2%). This m. p. is the same as that obtained by Meyer and Hohenemser for the methiodide derived from the partly unsaturated sulphide (*Helv. Chim. Acta*, 1935, **18**, 1061).

Dihydromyrcene.—Myrcene, prepared from bay oil (*Pimenta acris*) by the method of Power and Kleber (*Pharm. Rundschau*, 1895, **13**, 60), was reduced with sodium and alcohol as described by Semmler and Mayer (*Ber.*, 1911, **44**, 2010). The hydrocarbon, after being twice fractionally distilled over sodium, had b. p. 60°/16 mm., $n_D^{17°}$ 1·4542 (Found: C, 87·2; H, 12·9. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%).

Dihydromyrcene and Hydrogen Sulphide (*Sulphur Catalyst*).—A mixture of dihydromyrcene (69 g.), hydrogen sulphide (38 g.), and sulphur (0·5 g.) was heated in the autoclave for 20 hours at *ca.* 130°. On fractionation of the product the b. p. rose steadily from 50 to 90°/9 mm. and then from 68° to 80°/1 mm.; apart from unchanged dihydromyrcene, the distillate contained a mixture of isomeric monothiols, cyclic monosulphide (*ca.* 11 g.), and cyclic disulphide (2 g.), and a polymeric residue (1 g.) remained. The distillate fractions were extracted with 10% aqueous alkali in absence of air, and the extract after acidification was extracted with ether. Only a drop of liquid was thus obtained, but its odour was definitely mercaptan-like. Fractional distillation of the sulphide fractions gave a mixture of the $C_{10}H_{20}S$ isomers, (IV), (V), and (VI), b. p. 83°/9 mm., $n_D^{17°}$ 1·4858 (Found: C, 69·9; H, 11·4; S, 18·6. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%). With methyl iodide this product gave an oil, which on long standing yielded yellow crystals of the *methiodide*, m. p. 126—127° (decomp.) in insufficient quantity for complete purification (Found: I, 39·1. $C_{11}H_{23}I$ requires I, 40·3%). No pure *disulphide* was isolable but it was present to large extent in the higher fractions, such as one, b. p. 70°/1 mm., $n_D^{18·5°}$ 1·5202 (Found: C, 60·7; H, 10·0; S, 28·6. $C_{10}H_{20}S_2$ requires C, 58·8; H, 9·8; S, 31·3%).

A similar reaction between dihydromyrcene and hydrogen sulphide in the presence of sulphur, conducted at 160° for 22 hours, gave a product containing the $C_{10}H_{20}S$ isomers (15 g.), disulphide (3 g.), and polymeric compounds (1·5 g.).

The combined hydrocarbon fractions from the above experiments were again extracted with alkali, washed with water, dried (K_2CO_3), and distilled through a Fenske column. The recovered dihydromyrcene had b. p. 60°/16 mm., $n_D^{18°}$ 1·4511, and was shown by analytical and absorption-spectra measurements not appreciably to have cyclised or isomerised (Found: C, 87·2; H, 12·9; I.V., 362. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%; I.V., 368).

Geraniolene.—Citral was oxidised with silver oxide (Bernhauer and Forster, *J. pr. Chem.*, 1936, **147**, 199), and the resulting geranic acid was decarboxylated at 260—270° (Tiemann and Semmler, *Ber.*,

1893, **26**, 2724) to give geraniolene, b. p. 36°/10 mm., $n_D^{18°}$ 1·4408 (Found: C, 87·0; H, 12·9; I.V., 385. Calc. for C_9H_{16}: C, 87·1; H, 12·9%; I.V. 409). The low I.V. indicated the presence of some cyclised isomer.

Geraniolene and Hydrogen Sulphide (*Sulphur Catalyst*).—A mixture of geraniolene (70 g.), hydrogen sulphide (45 g.), and sulphur (0·5 g.) was heated in the autoclave for 24 hours at 150°. Distillation of the product gave a mixture of isomeric monothiols and cyclic monosulphide (12·5 g.), disulphide (1 g.), and a polymeric residue (1·5 g.). From the monosulphide fraction was obtained a pure mixture of the $C_9H_{18}S$ isomers (VII), (VIII), and (IX), b. p. 87°/16 mm., $n_D^{18°}$ 1·4812 (Found: C, 68·2; H, 11·4; S, 20·2. Calc. for $C_9H_{18}S$: C, 68·4; H, 11·4; S, 20·2%). Reaction of this product with methyl iodide at 15° gave an oil which would not solidify. The fraction containing the highest percentage of *disulphide* had b. p. 75°/1 mm., $n_D^{18°}$ 1·5100 (Found: C, 59·0; H, 10·1; S, 29·3. $C_9H_{18}S_2$ requires C, 56·9; H, 9·5; S, 33·7%).

Geraniolene and Hydrogen Sulphide (*Aluminium Sulphide Catalyst*).—A mixture of geraniolene (42 g.), recovered from the foregoing experiment), hydrogen sulphide (38 g.), aluminium sulphide (6 g.), and quinol (2 g.) was heated in the autoclave in the absence of air for 26 hours at *ca.* 150°. The product in ethereal solution was thoroughly extracted with 10% aqueous sodium hydroxide, washed with water, and dried (Na_2SO_4). On exposure to air the alkaline extract immediately started oxidising, with the formation of a viscous red oil (evidently a polymeric disulphide). Fractional distillation of the ethereal extract gave the $C_9H_{18}S$ isomeric mixture (5·2 g.), with b. p. ranging from 69—71°/11 mm., $n_D^{18°}$ 1·4729 (Found: C, 68·5; H, 11·2; S, 19·9; ·SH, 8·7%), to 80—81°/11 mm., $n_D^{18°}$ 1·4778 (Found: C, 67·9; H, 11·4; S, 20·3; ·SH, 12·3. Calc. for $C_9H_{18}S$: C, 68·4; H, 11·4; S, 20·2; ·SH, 0%. Calc. for C_9H_{17}·SH: ·SH, 20·9%). No disulphide was isolable, although one fraction (1·0 g.) contained a small proportion thereof (Found: S, 22·1. Calc. for $C_9H_{18}S$: S, 20·2. Calc. for $C_9H_{18}S_2$: S, 33·6%). An intermolecular sulphide fraction (0·5 g.), b. p. 117—122°/0·5 mm., $n_D^{18°}$ 1·4988, was isolated, and it appeared to be mainly the compound $C_9H_{17}S{\cdot}C_9H_{18}{\cdot}SH$ (see p. 1539) containing some $C_9H_{17}{\cdot}S{\cdot}C_9H_{17}$ (Found: C, 70·0; H, 11·1; S, 18·7. Calc. for $C_{18}H_{36}S_2$: C, 68·4; H, 11·4; S, 20·2%. Calc. for $C_{18}H_{34}S$: C, 76·6; H, 12·0; S, 11·3%).

Separation of the $C_9H_{18}S$ *isomers.* An approximately 0·2N-solution of cupric butyl phthalate (Turk and Reid, *loc. cit.*) was prepared by dissolving the reagent (5·1 g.) in 100 ml. of *n*-propyl alcohol containing acetic acid (5 ml.). This reagent was introduced into a solution of the $C_9H_{18}S$ mixture (3·3 g.) in *n*-propyl alcohol (50 ml.) until the green colour just persisted. After dilution with water to 800 ml. the product was extracted with chloroform, washed with water, dried, and fractionally distilled. After refractionation, 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (IX) (1 g.) was obtained as a colourless liquid, b. p. 64—66°/11 mm., $n_D^{18°}$ 1·4732 (Found: C, 68·4; H, 11·3; S, 19·9. Calc. for $C_9H_{18}S$: C, 68·4; H, 11·4; S, 20·2%).

Reaction of (IX) with methyl iodide at 0° gave only an oil, but when the sulphide was heated with excess of methyl iodide at 100° for 12 hours, yellow crystals separated, which after being washed with methanol and recrystallised from ethanol decomposed at *ca.* 200° and proved to be trimethylsulphonium iodide (Found: S, 15·7; I, 61·9. Calc. for C_3H_9SI: S, 15·7; I, 62·2%).

2 : 6-*Dimethylocta*-2 : 6-*diene.*—Geraniol was purified by conversion into its calcium chloride compound, and then reduced by sodium in liquid ammonia (Chablay; Dupont, Dulou, and Desreux, *locc. cit.*). After fractional distillation over sodium, the pure hydrocarbon had b. p. 56°/14 mm., $n_D^{17°}$ 1·4517 (Found: C, 87·0; H, 13·2; I.V., 370. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%; I.V., 368).

2 : 6-*Dimethylocta*-2 : 6-*diene and Hydrogen Sulphide* (*Normal Addition*).—A mixture of the olefin (69 g.), hydrogen sulphide (38 g.), and sulphur (0·5 g.) was heated in absence of oxygen under pressure for 22 hours at 140—150°. After extraction with aqueous alkali, fractional distillation of the product gave a mixture of $C_{10}H_{20}S$ isomers (5 g.) and a higher-boiling fraction which in this instance was not separated. Refractionation of the former yielded the $C_{10}H_{20}S$ isomers, b. p. 92—94°/18 mm., $n_D^{20°}$ 1·4842 (Found: C, 69·8; H, 11·5; S, 18·3. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%); this fraction contained about 11% of the monothiol (Found: ·SH, 2·1. Calc. for $C_{10}H_{19}SH$: ·SH, 19·2%). The unreacted olefin was recovered and shown to be uncyclised 2 : 6-dimethylocta-2 : 6-diene, b. p. 54°/13 mm., $n_D^{17°}$ 1·4501 (Found: C, 87·0; H, 13·2; I.V., 370. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%; I.V., 368).

In a further similar experiment 2 : 6-dimethylocta-2 : 6-diene (92 g.) was treated with hydrogen sulphide (58 g.) in the presence of aluminium sulphide (10 g.) for 23 hours at 150—165°. After extraction with 10% aqueous sodium hydroxide solution, the product was distilled as before to give the $C_{10}H_{20}S$ fraction (11 g., b. p. *ca.* 76—89°/9 mm.), disulphide (0·5 g., not isolable), and a residue of intermolecular sulphides (0·5 g.). On refractionation of the $C_{10}H_{20}S$ fraction, a product was obtained, b. p. 87—88°, n_D^{16} 1·4798 (Found: C, 69·6; H, 11·6; S, 18·6. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%), which contained *ca.* 27% of the monothiol 2(or 6)-mercapto-2 : 6-dimethyloct-6(or 2)-ene (Found: ·SH, 5·1. Calc. for $C_{10}H_{19}{\cdot}SH$: ·SH, 19·2%). Treatment of this product with copper butyl phthalate, in a manner analogous to that used for separation of the $C_9H_{18}S$ isomers, led to the isolation of 2 : 2 : 6-trimethyl-6-ethyl-tetrahydrothiopyran, b. p. 84°/10 mm., $n_D^{20°}$ 1·4792 (Found: C, 69·4; H, 11·5, S, 18·3. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%). Reaction with methyl iodide at 0—15° gave an oil which crystallised only extremely slowly, and reaction at 100° gave trimethylsulphonium iodide (Found: S, 15·7; I, 61·9. Calc. for C_3H_9SI: S, 15·7; I, 62·2%). By acidification of the alkali extract and subsequent extraction with ether was obtained 2 : 6-*dimercapto*-2 : 6-*dimethyloctane* (0·5 g.), b. p. 110°/9 mm., $n_D^{16°}$ 1·4971 (Found: C, 58·2; H, 10·6; S, 31·0; ·SH, 32·0. $C_{10}H_{22}S_2$ requires C, 58·3; H, 10·7; S, 31·0; ·SH, 32·0%).

In a third experiment a mixture of 2 : 6-dimethylocta-2 : 6-diene (77 g.), hydrogen sulphide (48 g.), aluminium sulphide (8 g.), and quinol (2 g.) was heated for 24 hours at *ca.* 150°. From the $C_{10}H_{20}S$ fraction (7·5 g.) was obtained a mixture of isomers, b. p. 86—8°/10 mm., $n_D^{20°}$ 1·4782 (Found: C, 69·7; H, 11·5; S, 18·7. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%), which contained 42% of the monothiol (Found: ·SH, 8·0. Calc. for $C_{10}H_{19}SH$: ·SH, 19·2%). Removal of the latter by the copper butyl phthalate method left somewhat impure 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran, b. p. 80—83°/11 mm., $n_D^{14°}$ 1·4806 (Found: C, 70·7; H, 11·6; S, 17·5. Calc. for $C_{10}H_{20}S$: C, 69·8; H, 11·6; S, 18·6%).

2 : 6-*Dimethylocta*-2 : 6-*diene and Hydrogen Sulphide* (*Abnormal Addition*).—Two Pyrex tubes, each containing the olefin (18·3 g.), hydrogen sulphide (5·1 g.), and acetone (1·2 g.), were sealed under vacuum and irradiated with U.V. light at 15° for 4 hours. After extraction with 10% aqueous alkali, the product was fractionally distilled to give a $C_{10}H_{20}S$ isomeric mixture (9 g.) and intermolecular sulphides (2 g.). From the former was obtained a fraction, b. p. 92—92·5°/11 mm., $n_D^{19\cdot5°}$ 1·4767 (Found : C, 69·8; H, 11·6; S, 18·6. Calc. for $C_{10}H_{20}S$ requires C, 69·8; H, 11·6; S, 18·6%), which contained 56% of the monothiol, 3(or 7)-mercapto-2 : 6-dimethyloct-6(or 3)-ene (Found : ·SH, 10·8. $C_{10}H_{19}$·SH requires ·SH, 19·2%). Removal of the thiol by the copper butyl phthalate method left 2 : 3-*dimethyl*-6-iso*propyl*-*tetrahydrothiopyran*, b. p. 46°/1 mm., $n_D^{18°}$ 1·4831 (Found : C, 69·7; H, 11·5; S, 18·2. $C_{10}H_{20}S$ requires C, 69·8; H, 11·6; S, 18·6%). Acidification of the alkaline extract liberated 3 : 7-*dimercapto*-2 : 6-*dimethyloctane*, b. p. 132°/11 mm., $n_D^{17°}$ 1·5025 (Found : C, 58·3; H, 11·0; S, 30·8. $C_{10}H_{22}S_2$ requires C, 58·3; H, 10·7; S, 31·0%). Fractionation of the intermolecular sulphide fraction led to the separation of 5(or 2)-*mercapto*-1 : 2 : 6-*trimethylheptyl* 4-*methyl*-1-iso*propylhex*-4-*enyl sulphide* or the 1 : 5-*dimethyl*-1-*ethylhex*-4-*enyl sulphide* (as XV), b. p. 147°/0·1 mm., $n_D^{18\cdot5°}$ 1·4990 (Found : C, 69·4; H, 11·6; S, 18·8; ·SH, 10·0. $C_{20}H_{40}S_2$ requires C, 69·8; H, 11·6; S, 18·6; ·SH, 9·6%).

Nitrous Acid Test for Thiols.—Dilute sulphuric acid was slowly added to an alcoholic solution of the thiol containing solid sodium nitrite, through which nitrogen was bubbling (Rheinboldt, *loc. cit.*). All the products of normal addition of hydrogen sulphide to dihydromyrcene and 2 : 6-dimethylocta-2 : 6-diene gave green oils which appeared red in bulk when viewed by transmitted light; this was indicative of the tertiary grouping CRR'R''·SH. The U.V.-light-catalysed reaction product gave a bright red oil indicating the secondary grouping CHRR'·SH (the formation of a primary thiol not being feasible in this reaction), and the geraniolene products a reddish oil, which pointed to the presence of at least some secondary thiol.

Rubber and Hydrogen Sulphide (*Abnormal Addition*).—A 1% benzene solution of sol rubber was shaken with hydrogen sulphide in absence of air, and irradiated in a quartz flask with ultra-violet light for 4 hours. The product after separation by precipitation with alcohol and drying in a high vacuum contained 1·1% of sulphur. The experiment was repeated using as solvent benzene containing 5% of acetone as photosensitiser. From two runs the products contained 2·25 and 2·65% of sulphur severally; a very small quantity of rubber came out of solution as a gel, and in the latter case this contained 10·1% of sulphur. When crepe containing its natural antioxidants was used, the sulphur value obtained was 0·8%. Seven hours' irradiation of a 9% solution of milled acetone-extracted crepe in benzene containing 5% of acetone gave small quantities of gels containing 4·5—2·2% of sulphur, and a main product with 1% (*M*, 153,000). The same conditions, 1% solutions being used without irradiation, led to incorporation of only 0·15% of sulphur. A further solution was saturated with hydrogen sulphide at 0° and then heated with benzoyl peroxide for 1 hour at 75°; this increased the sulphur intake to 0·30%.

Milled acetone-extracted crepe (0·5 g.) and liquid hydrogen sulphide (30 ml.) were sealed in a Pyrex tube. After 3 days with occasional gentle shaking the rubber pased into solution, and was then irradiated for 25 minutes at 15°; the product contained 2·07% of sulphur. On repetition of the experiment with milled crepe (0·7 g.), hydrogen sulphide (24 ml.), and acetone (1·2 ml.), the rubber did not go wholly into solution. The analyses of the two portions after 25 minutes irradiation were : Found, for insoluble fraction, C, 85·6; H, 11·6; S, 1·3; ash, 0·17; 0 (diff.), 1·3%. Found, for soluble fraction, C, 85·0; H, 11·65; S, 3·2; ash, 0·09; 0 (diff.), 0·06%. It is evident that liquid hydrogen sulphide preferentially dissolved the pure hydrocarbon, as the starting material contained 1·0% of oxygen.

Rubber and Hydrogen Sulphide (*Normal Addition*).—Similar 1-mm. sheets (10 g.) of crepe rubber, milled alone and with ½% of sulphur, were heated with hydrogen sulphide (24 g.) in the autoclave in absence of air for 2 hours at 140°. The products, although full of small hydrogen sulphide bubbles, were elastic like sulphur-vulcanised rubber (Found, for uncatalysed product; S, 1·9: 2·2. For catalysed product : S, 2·7, 2·8%). After a similar reaction at 140—160° the products were acetone-extracted to remove free sulphur (Found, for uncatalysed product : S, 2·75. For catalysed product : S, 3·25%); at this temperature acetone-extracted crepe rubber reacted to give a product (Found : S, 3·15%) after further acetone-extraction. Reaction of milled crepe (10 g.) with hydrogen sulphide (24 g.) for 2 hours at 260° yielded a product in which some chain fission had obviously taken place (Found : S, 8·5%). Sheets of milled crepe with and without ½% of sulphur were heated at 140° for 48 hours in hydrogen sulphide at atmospheric pressure (Found, for uncatalysed product : S, 0·5; for catalysed product, S, 0·8%); a control sample heated in nitrogen was unchanged.

An 8% solution (250 ml.) of milled acetone-extracted crepe rubber in *cyclo*hexane, liquid hydrogen sulphide (50 g.), ferrous sulphide (4 g.), and ferric oxide (2 g.) were sealed in the autoclave in absence of air and heated for 20 hours at 85—103°. Some rubber (3—4 g.) came out of solution as a gel (Found : S, 4·8%). The main solution was centrifuged to remove catalyst, and the rubber precipitated by alcohol (Found : S, 1·1%).

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300. *The Application of Infra-red Analysis to the Study of the Reaction of Certain Olefins with Hydrogen Sulphide.*

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The method of infra-red analysis has been used to investigate the reaction of geraniolene and dihydromyrcene with hydrogen sulphide in the presence of catalysts that usually promote "normal" addition to the double bond according to the Markovnikov rule. It has been possible to show conclusively that under these conditions both the hydrocarbons give mono-addition products which consist partly of cyclic sulphides, geraniolene giving rise to 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran, and dihydromyrcene to 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran. Such products could only have been formed by "normal" addition reactions. The products of the reaction of hydrogen sulphide with dihydromyrcene under conditions favouring "abnormal" addition gave very different spectra.

In order to apply the infra-red method it was necessary first to establish rules for the spectroscopic identification of certain hydrocarbon groups. These rules are briefly discussed.

In the preceding paper Naylor has described an investigation of the reaction of hydrogen sulphide with the hydrocarbons geraniolene and dihydromyrcene. Many of the conclusions relating to the structures of the reaction products came from an investigation of their infra-red spectra. The purpose of this paper is to present in detail the evidence for these conclusions.

Infra-red analysis can be used in two ways to establish the structure of a reaction product. In the first place, any chemical bond or group that has characteristic infra-red absorption bands can be detected, and while in most cases this does not establish the structure it may enable one to eliminate some of the possible formulations and give strong presumptive evidence for a particular one. The second and more conclusive method is to compare the spectrum of the reaction product with that of a specially synthesised specimen of the compound postulated as the reaction product. Both methods have been used in the present investigation, the first two sections of which are concerned with the material required for the first method, while the third contains the combined application of both methods to the problem in hand.

Chemical Groupings and their Characteristic Absorption Bands.—The various characteristic group frequencies that we shall use in the examination of the reaction products are given in Table I, where R represents an alkyl group. Most of these correlations are well established

Table I.

Chemical grouping.	Type of vibration.	Frequency in cm.$^{-1}$.
SH	SH valence	2500—2650
CH_2 and CH_3	CH deformation	1430—1470
CH_3	CH deformation	1370—1375
$C<^{CH_3}_{CH_3}$	CH deformation	*ca.* 1360 and 1380 *
$RR'C{:}CH_2$	C=C valence	1645—1655 *
$RR'C{:}CH_2$	CH deformation	885— 895
$RR'C{:}CHR''$	C=C valence	1670—1680 *
$RR'C{:}CHR''$	CH deformation	800— 840

(see, *e.g.*, Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand Co. Inc., 1946; Barnes, Gore, Liddel, and Williams, "Infra-red Spectroscopy," Reinhold, 1944; Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246), but those marked with an asterisk, which are more precise characterisations of older correlations, have recently been established in this laboratory and full details will be published elsewhere.

Both the C=C valence and the C—H deformation absorptions of the disubstituted ethylenes have considerably higher extinction coefficients than the corresponding absorptions of the trisubstituted compounds. This is important if such absorptions are used to estimate the relative amounts of the two types of grouping in a mixture of both.

The Spectra of the Olefins.—The two hydrocarbons originally used for the reaction with hydrogen sulphide were geraniolene and dihydromyrcene. Their spectra are shown in Fig. 1, and in this and the subsequent figures absorption bands mentioned in the text are accented by a line down the middle in the appropriate spectra.

Geraniolene is considered to be mainly 2 : 6-dimethylhepta-1 : 5-diene,

$$CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2,$$

although its method of preparation (Bernhauer high-temperature decarboxylation; see Naylor, *loc. cit.*) does not exclude the possibility of considerable amounts of other isomers. Its infra-red spectrum has absorption bands at 1654 and 891 cm.$^{-1}$, and at 1680 and 821 cm.$^{-1}$ which

can be ascribed to C=C valence and C—H deformation vibrations respectively of $RR'C{:}CH_2$ and $RR'C{:}CHR''$ groups, in agreement with the above formula (see Table I).

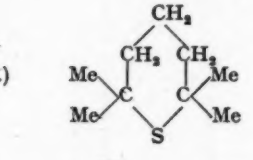
Dihydromyrcene is generally assumed to consist largely of 2 : 6-dimethylocta-2 : 6-diene, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, but its method of preparation (Naylor, *loc. cit.*) suggests that the isomers 2 : 6-dimethylocta-1 : 6-diene, $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, and 6-methyl-2-ethylhepta-1 : 5-diene,

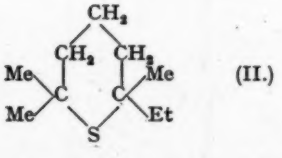
$$CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CEt{:}CH_2,$$

may also be present. Comparison of the spectrum of this material with that of pure 2 : 6-dimethylocta-2 : 6-diene, prepared by an independent method, shows that in addition to the usual bands attributable to the $RR'C{:}CHR''$ groups (at 1678 and 820 cm.$^{-1}$) there are also bands (at 1650 and 889 cm.$^{-1}$) attributable to the $RR'C{:}CH_2$ groups of these alternative isomers. For this reason the dihydromyrcene used in the earlier experiments with hydrogen sulphide and sulphur catalyst was subsequently replaced by the pure 2 : 6-dimethylocta-2 : 6-diene.

Infra-red Analysis of the Reaction Products.—(1) *General.* The chemical aspects of the reactions of geraniolene and dihydromyrcene with hydrogen sulphide have been fully discussed by Naylor (*loc. cit.*). The spectroscopic problem was to investigate certain portions of the products obtained with catalysts that promote " normal " addition according to the Markovnikov rule. In particular we required to establish the presence or absence of 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (I) and 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (II) as reaction products of the respective hydrocarbons.

(I.)





(II.)

We also investigated some products from similar reactions in which the conditions were such that products of " abnormal " addition were to be expected.

The spectra of the reaction products of geraniolene and hydrogen sulphide obtained under conditions of normal addition are given in Fig. 2, the steps in the gradual purification and identification being indicated by the following key: (A) Spectrum of the reaction product, sulphur being used as catalyst. (B) Spectrum of the reaction product, aluminium sulphide being used as catalyst (to avoid the possibility of the catalyst reacting with the hydrocarbon). (C) Spectrum of B after removal

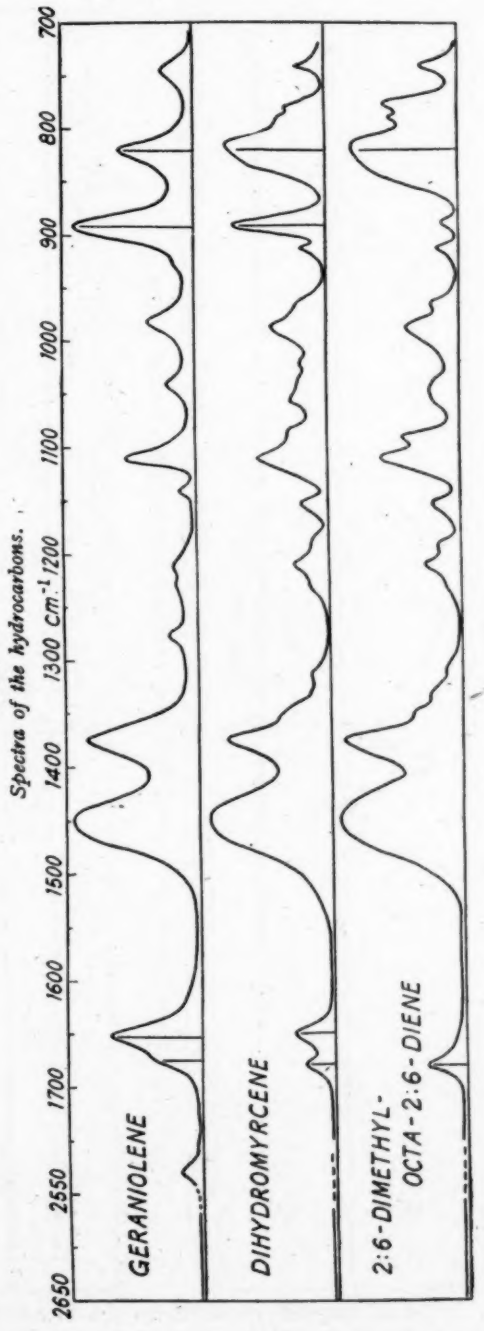


FIG. 1.
Spectra of the hydrocarbons.

of thiols by cupric butyl phthalate. (S) Spectrum of synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran.

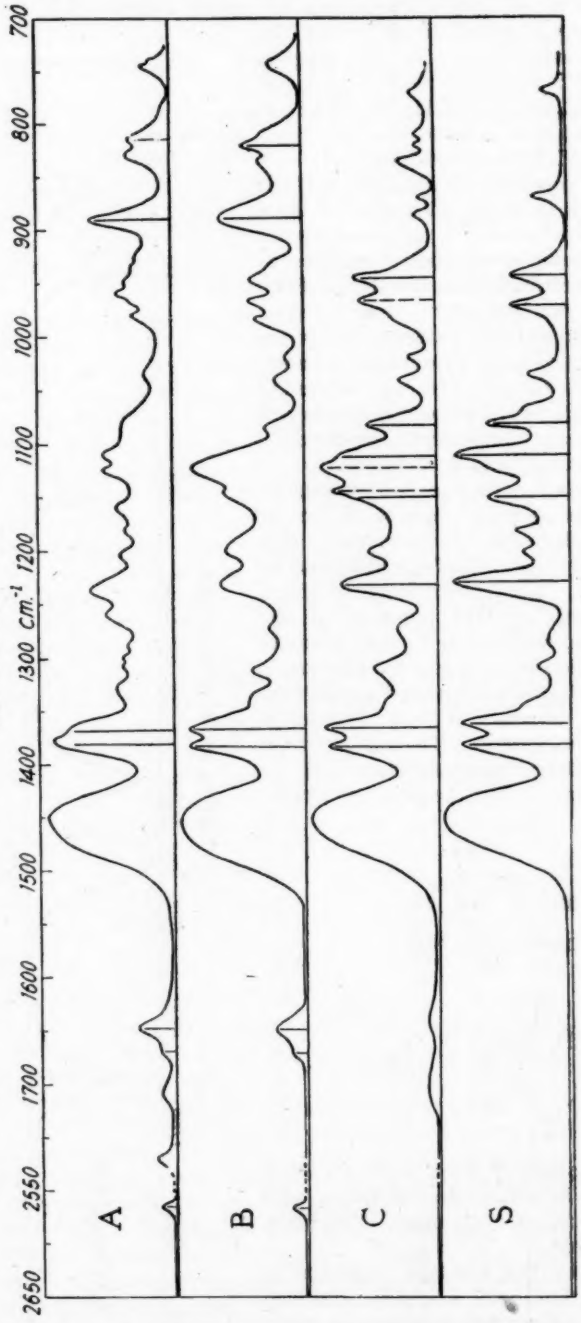


FIG. 2.

Spectra of the "normal" geraniolene–hydrogen sulphide reaction products and of 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (Spectrum S).

The corresponding spectra for the dihydromyrcene reaction are given in Fig. 3, but it should be noted that only (A) refers to the reaction with dihydromyrcene; the remaining spectra are all of products obtained by using the synthetic specimen of the single isomer 2 : 6-dimethylocta- 2 : 6-diene of which the spectrum is given in Fig. 1. It should also be noted that (B′) of Fig. 3 is the spectrum of a reaction product obtained under the same conditions as (B) but

with some quinol present to remove any peroxides. As in the case of the geraniolene products, (C) and (S) denote respectively the thiol-free product and the independently synthesised cyclic sulphide.

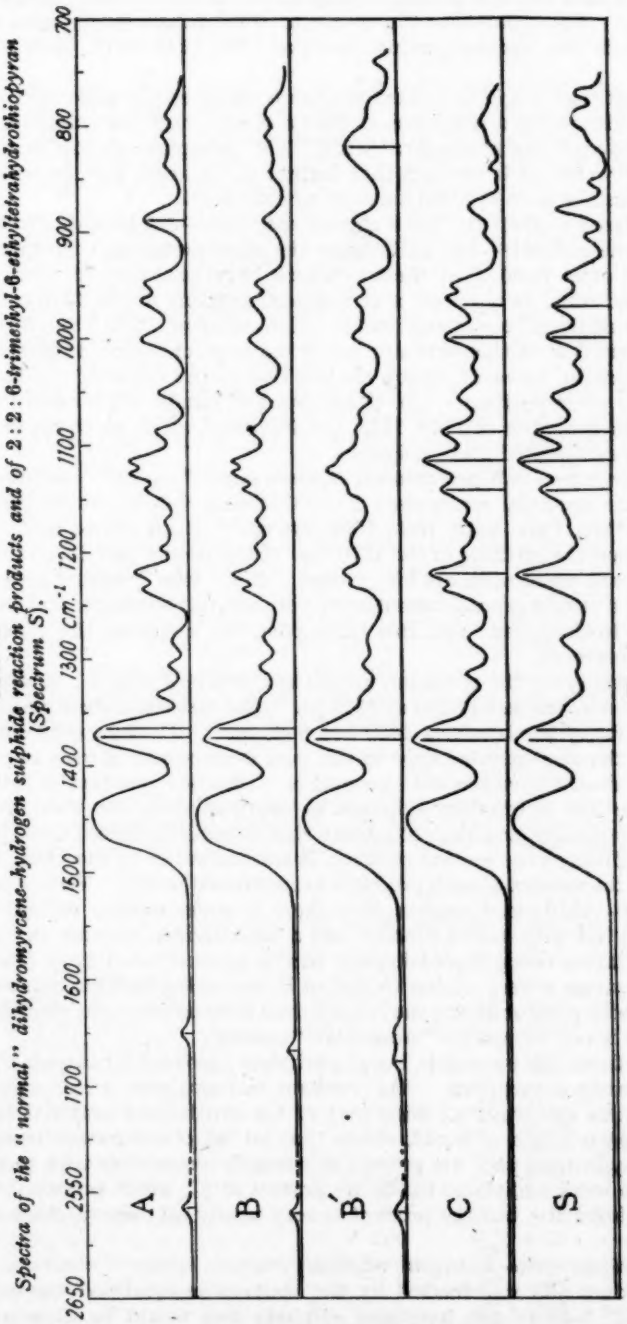


FIG. 3. *Spectra of the "normal" dihydromyrcene–hydrogen sulphide reaction products and of 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (Spectrum S).*

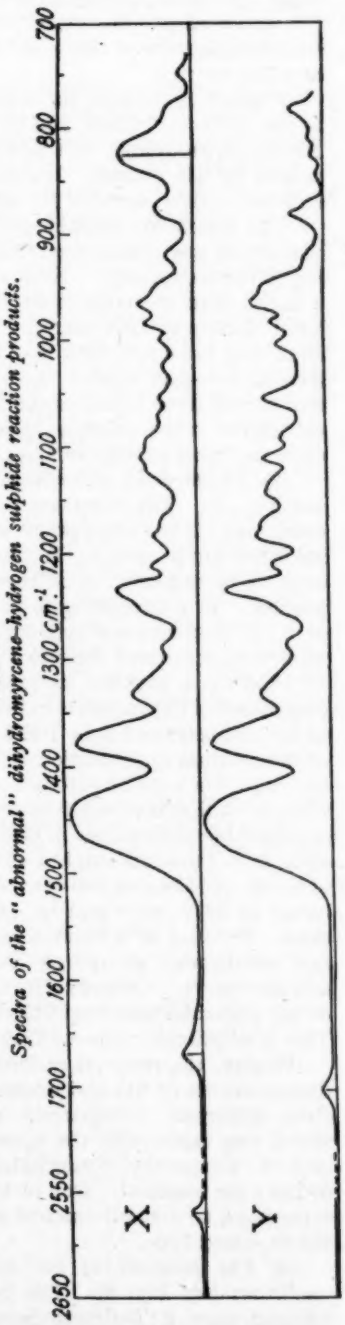


FIG 4. *Spectra of the "abnormal" dihydromyrcene–hydrogen sulphide reaction products.*

In Fig. 4 are represented the spectra of the products obtained when 2 : 6-dimethylocta-2 : 6-diene and hydrogen sulphide are irradiated with ultra-violet light—conditions that should promote abnormal addition: (X) is the original unpurified product, and (Y) the thiol-free material.

(2) *The products of the geraniolene–hydrogen sulphide reaction under "normal" conditions* (see Fig. 2). The expected product—2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran—has four methyl groups that occur in pairs, and this should give rise to the splitting of the 1370 cm.$^{-1}$ band. Such a splitting (1381 and 1362 cm.$^{-1}$) is found in the spectrum of the synthetic material (S), and confirms its authenticity. Other bands in the spectrum of (S) which can be used for the identification of this sulphide in the reaction product occur at 1229, 1149, 1111, 1079, 971, and 942 cm.$^{-1}$.

Product A (sulphur as catalyst) has a poorly defined spectrum which shows little splitting of the 1370 cm.$^{-1}$ band, and in addition has absorptions at 1648 and 889 cm.$^{-1}$ characteristic of $RR'C{:}CH_2$ groupings, 1670 and 815 cm.$^{-1}$ characteristic of $RR'C{:}CHR''$ groupings, and 2570 cm.$^{-1}$ caused by SH groups. In other words, it is obvious that further purification was necessary, and that at least some of the impurities were residual amounts of monothiol.

The aluminium sulphide-catalysed product (B) has a cleaner spectrum—due probably to the absence of any sulphur–geraniolene products—but still retains the other groupings corresponding to the monothiols. However, after removal of these by cupric butyl phthalate (product C) a fairly clean spectrum is obtained with, as required, a pronounced splitting of the 1370 cm.$^{-1}$ band (1381 and 1363 cm.$^{-1}$). In addition, the strong bands which occur at 1231, 1150, 1111, 1082, and 945 cm.$^{-1}$ show that there is a considerable amount of the expected sulphide present. Several well-pronounced bands remain, however, which are not due to the expected product, and one of these obscures the 971 cm.$^{-1}$ position. The three strongest bands which cannot be attributed to this sulphide have their centres at 1144, 1122, and 965 cm.$^{-1}$, all of which are very close to strong absorptions of the synthesised cyclic sulphide.

(3) *The products of the dihydromyrcene–hydrogen sulphide reaction under "normal" conditions* (see Fig. 3). The spectrum of the specially synthesised 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran (S) has absorptions at 1220, 1142, 1116, 1087, 1002, 970 cm.$^{-1}$ which can be used for identification purposes. In this case the splitting of the 1370 cm.$^{-1}$ band is only just detectable, as is to be expected, since there are equal numbers of "paired" and "lone" methyl groups present. It is interesting to note a strong general resemblance between this spectrum and that of 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran, and this correspondence confirms the closely related structures of these two substances.

Product A (sulphur as catalyst) gives the spectrum shown at the top of Fig. 3. A small proportion of SH groups is indicated by the usual band at 2570 cm.$^{-1}$, and also some unsaturation of the disubstituted type $RR'C{:}CH_2$ by the bands at 1650 and 889 cm.$^{-1}$. The fact that some of the residual unsaturation is of the disubstituted type in this case is surprising in view of the fact that the initial hydrocarbon should have few such groupings. However, product B (with pure 2 : 6-dimethylocta-2 : 6-diene and aluminium sulphide as catalyst) does not show any considerable absorptions in these positions, and the probability that this disubstituted unsaturation is due to some sulphur–dihydromycene reaction products is substantiated by the presence of bands at 1650 and 890 cm.$^{-1}$ in the spectra of such products (unpublished work). Very weak bands at 2570 cm.$^{-1}$ and *ca.* 1660—1670 cm.$^{-1}$ suggest that there is some residue including thiol. Product B′ (obtained as B but with quinol present) has a considerable number of SH and unsaturated groupings—the latter being predominantly of the trisubstituted type (1680 and 820 cm.$^{-1}$). Otherwise its spectrum is very similar to that of B, indicating that the removal of any peroxides that might have been present during the reaction had little effect on the product. This is additional evidence that it is not formed by "abnormal" addition.

Finally, the removal of thiol from (B) by cupric butyl phthalate (product C) caused the disappearance of SH and unsaturation absorptions. The resultant material gives a reasonably clean spectrum. Comparison of this spectrum (C) with that of the synthesised material (S) which was taken with the same path-length of liquid, shows that all the characteristic bands of 2 : 2 : 6-trimethyl-6-ethyltetrahydrothiopyran are present in strength comparable with those of the pure material. One or two weak additional bands are present in (C) which presumably correspond to a small amount of impurity, but the product is very nearly all pure sulphide of the expected type.

(4) *The products of the dihydromyrcene–hydrogen sulphide reaction under "abnormal" conditions* (see Fig. 4). The product (X) was formed by the ultra-violet-catalysed reaction between pure 2 : 6-dimethylocta-2 : 6-diene and hydrogen sulphide and would be expected to be "abnormal" in type. It has a very different spectrum from those products discussed in the preceding section although it does have bands at 2580 cm.$^{-1}$ (SH groups) and at 1670 and 825 cm.$^{-1}$ characteristic of trisubstituted double bands. This means that there is a considerable proportion of monothiol present. Removal of this by the usual method gave product

(Y), which has a spectrum similar to (X) except that the above three bands have disappeared. There remains a weak band near 1700 cm.$^{-1}$ which is probably due to some impurity introduced during the removal of thiol, as such a frequency is characteristic of C=O rather than C=C groups. The spectrum of this sample is completely different from that of the final " normal " product of Section (3).

Discussion.

We have shown that the spectra of the reaction products under conditions favouring " normal " addition are extremely similar to those of 2 : 2 : 6 : 6-tetramethyl- and 2 : 2 : 6-trimethyl-6-ethyl-tetrahydrothiopyran, but there are certain discrepancies which must be considered before this strong resemblnce can be accepted as conclusive proof of the identities of the reaction products. When spectra differ in this way it may be either because impurities are present, or because the compounds of which the spectra are being compared are really different, but of closely related structure. These two cases, which we shall call (1) and (2), can usually be distinguished. In the former, the main bands of the pure compound should be stronger than the corresponding bands in the unknown for the same cell thickness, unless, of course, a band due to the impurity overlaps one of these " key " bands. From Figs. 2 and 3 it will be seen that this is indeed the case for our comparisons. Again, in case (1) all bands, except the very weakest, detectable in the spectrum of the pure compound should be present in the unknown, whereas in case (2) the number of weak bands may be greater for the pure compound than the unknown. It will be seen that on this criterion also our identification is justified, for although there is one weak band in 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran (near 1180 cm.$^{-1}$) which does not appear in the (C) spectrum (Fig. 2), this sole exception may well be due to a trace of impurity in the synthetic compound.

In the case of the comparison of the geraniolene product with the synthetic 2 : 2 : 6 : 6-tetramethyltetrahydrothiopyran, it is obvious that the amount of " impurity " is considerable and it is thought that this arises from the presence of other isomers than 2 : 6-dimethylhepta-1 : 5-diene in the original hydrocarbon. The dihydromyrcene product has relatively little impurity, in agreement with the fact that pure 2 : 6-dimethylocta-2 : 6-diene was used for the reaction.

We wish to draw attention in this connection to the power of the infra-red method in detecting by-products in a reaction. The difficulty of sufficiently purifying the product to enable us to use infra-red analysis is a sufficient indication of this, and of the precision of the identification once that purification has been achieved.

Experimental.

The infra-red spectra were taken with the Hilger Double-Beam Spectrometer described by Sutherland and Thompson (*Trans. Faraday Soc.*, 1945, **41**, 174). They were recorded under double-beam conditions so that the absorption of radiation by water vapour in the atmosphere did not interfere with the spectra.

Table II.

Analytical data for the samples investigated spectroscopically.

Compound.	B. p.	Refractive index.	Found, %. C.	Found, %. H.	Found, %. S.	Calculated, %. C.	Calculated, %. H.	Calculated, %. S.
Geraniolene	36°/10 mm.	$n_D^{18°}$ 1·4408	87·0	12·9	—	87·1	12·9	—
Dihydromyrcene.....	60 /16 mm.	$n_D^{17°}$ 1·4542	87·2	12·9	—	87·0	13·0	—
2 : 6-Dimethylocta-2 : 6-diene	56 /14 mm.	$n_D^{17°}$ 1·4517	87·0	13·2	—	87·0	13·0	—
Geraniolene products A ...	86—87 /16 mm.	$n_D^{18°}$ 1·4812	68·2	11·4	20·2	68·4	11·4	20·2
,, ,, B ...	69—71 /11 mm.	$n_D^{18°}$ 1·4729	68·5	11·2	19·9	,,	,,	,,
,, ,, C ...	66 /11 mm.	$n_D^{18°}$ 1·4732	68·2	11·3	19·9	,,	,,	,,
,, ,, S ...	66 /12 mm.	$n_D^{19°}$ 1·4763	68·3	11·6	20·1	,,	,,	,,
" Normal " dihydromyrcene products A	83 /9 mm.	$n_D^{17°}$ 1·4858	69·9	11·4	18·6	69·8	11·6	18·6
,, B	87—88 /9 mm.	$n_D^{16°}$ 1·4798	69·6	11·6	18·6	,,	,,	,,
,, B'	86—88 /10 mm.	$n_D^{20°}$ 1·4782	69·7	11·5	18·7	,,	,,	,,
,, C	84 /10 mm.	$n_D^{20°}$ 1·4792	69·4	11·5	18·3	,,	,,	,,
,, S	87 /13 mm.	$n_D^{20°}$ 1·4849	69·6	11·7	18·6	,,	,,	,,
" Abnormal " dihydromyrcene products X.....	92 /11 mm.	$n_D^{19·5}$ 1·4767	69·8	11·6	18·6	69·8	11·6	18·6
,, Y	46 /1 mm.	$n_D^{18°}$ 1·4831	69·7	11·5	18·2	,,	,,	,,

A rock-salt prism was used throughout for this work, and the effective slit-widths (in cm.$^{-1}$) were 40 at 2000 cm.$^{-1}$, 12 at 1600 cm.$^{-1}$, 6 at 1000 cm.$^{-1}$, and 5 at 700 cm.$^{-1}$. The positions of the bands are accurate to 2 cm.$^{-1}$ up to 1300 cm.$^{-1}$, 4 cm.$^{-1}$ from 1300 to 1900 cm.$^{-1}$, and 20 cm.$^{-1}$ at any higher frequencies in this work.

The experimental details of the olefin–hydrogen sulphide reactions have been given by Naylor (*loc. cit.*) and it will suffice here to give the physical properties and analytical figures for the samples investigated. These figures were obtained by Naylor at Welwyn, and the samples were then sealed in nitrogen and transmitted to Cambridge. The spectra were taken in a rock-salt cell of 0·06 mm. thickness, immediately after the samples had been unsealed.

Our thanks are due to Drs. E. H. Farmer and R. F. Naylor, of the British Rubber Producers' Research Association, for bringing this problem to our notice, and for providing us with all the specimens investigated. We are also grateful to them for much helpful discussion during the course of the work.

One of us (N. S.) is indebted to St. Catharine's College, and the Dunlop Rubber Co. Ltd., for financial help during this investigation. The spectrometer used was provided by a joint grant from the Royal Society and Imperial Chemical Industries Ltd.

LABORATORY OF COLLOID SCIENCE, CAMBRIDGE. [*Received, February 6th*, 1947.]

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301. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part III. The Reaction of Sulphur with Squalene.*

By GEORGE F. BLOOMFIELD.

Sulphur reacts with squalene in a manner very similar to that observed with dihydromyrcene, and an intramolecularly-linked unimolecular sulphide as well as an intermolecularly-linked polysulphide is obtained.

RATHER prolonged reaction times are necessary to obtain an appreciable degree of sulphuration of squalene, H·[CH$_2$·CMe:CH·CH$_2$]$_3$[CH$_2$·CH:CMe·CH$_2$]$_3$·H, below 140° in the absence of auxiliary activating substances, and, as might be expected, the course of the reaction shows a marked resemblance to the sulphuration of dihydromyrcene. The crude reaction product consists of unreacted squalene of undiminished olefinic unsaturation, together with a unimolecular sulphurated product and a bimolecular polysulphide. Of the two sulphurated components, the unimolecular product, which cannot be completely freed from unreacted squalene, is present in the major proportion, although the sulphur which enters into reaction is distributed fairly equally among the two components. The unimolecular product, $C_{30}H_{50}S$, in which one sulphur atom has become incorporated in the squalene molecule with the loss of one double bond, is substantially free from sulphydryl sulphur, and contains carbon and hydrogen in the same ratio as in the original hydrocarbon. The bimolecular product is a polysulphide of squalene, $C_{60}H_{100}S_6$, of considerable stability towards sodium sulphite, and the ratio of hydrogen to carbon is again that of the parent hydrocarbon; the incorporation of sulphur is accompanied by loss of olefinic unsaturation. The unsaturation of the bimolecular product undergoes a further reduction on heating at temperatures exceeding 140°.

In view of the known sensitivity of the reaction of sulphur with olefins towards quite small proportions of certain activating substances, it is of considerable interest that the addition of mercaptobenzthiazole and a zinc soap to the sulphur–squalene system results only in increased yields in both uni- and bi-molecular products without greatly affecting their relative proportions, provided that the time and temperature conditions of the reaction remain unaltered.

EXPERIMENTAL.

Microanalyses were carried out by Dr. W. T. Chambers and Miss H. Rhodes. Olefinic unsaturation was determined by bromine addition (Bloomfield, *J. Soc. Chem. Ind.*, 1945, **64**, 274), and molecular weights were determined by depression of f. p. of benzene.

Squalene (14 g.) was heated with sulphur (1·4 g.) in an atmosphere of nitrogen for 3 hrs. at 140°. The product was freed from unreacted sulphur first by cooling and filtering, and finally by passage through a falling-film molecular still (Farmer and Sutton, *ibid.*, 1946, **65**, 164) at 100°. Subsequent molecular distillation of the product at 140° gave a pale yellow distillate (13 g.) having $n_D^{17°}$ 1·5031 (Found: C, 86·1; H, 12·0; S, 2·1; ·SH, 0·09; I.V., 338; *M*, 412. Calc. for mixture of 71% $C_{30}H_{50}$ and 29% $C_{30}H_{50}S$: C, 85·7; H, 12·2; S, 2·1; I.V. 348; *M*, 420) which showed selective U.V. absorption at 2800 A., and a reddish-brown viscous residue (1·5 g.) (Found: C, 71·15; H, 9·95; S, 18·75; ·SH, 0·3; I.V., 250 ± 15; *M*, 825. $C_{60}H_{100}S_6$ requires C, 71·1; H, 9·95; S, 18·95%; *M*, 1013). A 10% aqueous solution of sodium sulphite removed 9% of the sulphur contained in the residue in 3 hrs. at 100°, but was without action on the sulphur in the distillate. A sample of the residue was heated in a vacuum for 45 mins. at 160° (Found: C, 70·9; H, 9·9; S, 18·7; ·SH, 0·9%; I.V., 209). Further molecular distillation of the distillate at 110° yielded fractions respectively poorer (Found: S, 1·2%)

and richer (Found : S, 4·8%; *M*, 415) in the sulphurated component. The former of these two fractions yielded substantially pure squalene, $n_D^{29°}$ 1·4988 (Found : S, 0·4%; I.V., 360) on passage through chromatographic alumina on which the sulphurated component was strongly adsorbed.

Squalene (10 g.), sulphur (1·0 g.), zinc oxide (0·5 g.), stearic acid (0·5 g.), and mercaptobenzthiazole (0·1 g.) were heated together for 3 hrs. at 140°. Separative treatment in the molecular still yielded a distillable component (8·4 g.), $n_D^{19°}$ 1·5109 (Found : C, 83·15; H, 11·6; S, 5·3; active H, <0·01; I.V., 312; *M*, 413. Calc. for 73% $C_{33}H_{56}S$ + 27% $C_{30}H_{50}$: C, 83·1; H, 11·7; S, 5·3%; I.V., 311; *M*, 434) and a residue (1·0 g.) (Found : S, 19·95%) which was free from zinc.

This paper forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The author expresses his thanks to Dr. E. H. Farmer for his advice and criticism.

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
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[*Received, January 15th,* 1947.]

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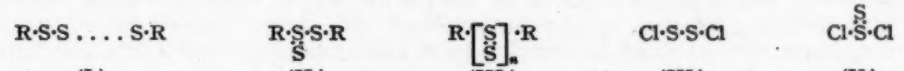
302. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part IV. The Thermal Decomposition of Organic Polysulphides, and its Contribution to the Sulphur–Olefin Reaction.*

By GEORGE F. BLOOMFIELD.

At temperatures in the region of 140° organic polysulphides undergo disproportionation resulting from thermal fission of S–S bonds and recombination of the fission products. In the presence of olefins a considerable proportion of the fission products become attached to ethylenic centres of the olefin, forming mixed mono- and poly-sulphides. The major part of the monosulphide product is fully saturated, hydrogen-capture occurring during, or subsequent to, the formation of adducts from the olefin and sulphurated fragments; unsaturation, however, appears in the polysulphide portion. The polysulphides are capable of producing monothio-cross-links between the original olefinic molecules only in so far as they are able to yield up elementary sulphur to the olefin, and when the original olefin is a polyisoprene the tendency towards the formation of a high proportion of intramolecular cyclic sulphide still further reduces the opportunity for formation of intermolecular sulphur-cross-linked products.

SINCE polysulphides are the principal products of the reaction of sulphur with olefins (Farmer and Shipley, Part I, this vol., p. 1519) an understanding of their thermal stability and of their further reaction with olefins is clearly of importance in clarifying the general problem of chemical changes associated with the olefin–sulphur reaction and the related problem of rubber vulcanisation.

The structure of polysulphides has long presented difficulty in respect of the necessity for deciding between their representation by the wholly linear structures (I) or by co-ordinated structures of type (II) or (III). Based principally on evidence provided by *X*-ray data (Katz,



(I.) (II.) (III.) (IV.) (V.)

Trans. Faraday Soc., 1936, **32**, 77) and by the lability of a considerable proportion of the sulphur atoms on treatment with alkali (Patrick, *ibid.*, p. 347) or with sodium sulphite (Parker, *India Rubber J.*, 1945, **108**, 387), a co-ordinated structure has been generally assigned to those polysulphides obtained by the interaction of organic halides and alkali polysulphides. Evidence based on the lability of sulphur atoms is, however, no certain criterion of the presence of co-ordinated sulphur atoms, since it is now shown that a comparable lability is exhibited by *two* of the four sulphur atoms in tetrasulphides obtained by the interaction of thiols and sulphur monochloride. Whether one accepts a linear (IV) or branched (V) structure for sulphur monochloride, it follows that three of the four sulphur atoms of the derived tetrasulphide must be in a linear chain, so that when two sulphur atoms are removed, at least one of them must have been abstracted from a linear chain. The electron-diffraction investigations of Palmer (*J. Amer. Chem. Soc.*, 1938, **60**, 2360) indicate the linear structure (IV) for the monochloride, and since, moreover, a recent ultra-violet absorption study by Koch (in the press) provides convincing evidence of a linear structure of some of the organic polysulphides which form the basis of the present work, it seems fully justifiable to assume linear structures both for the tetrasulphides prepared by the interaction of thiols with sulphur monochloride and for the polysulphide products of the sulphur–olefin reaction. The chemical behaviour of these poly-

sulphides is not at variance with the assumption of a linear structure, nor is a linear structure inconsistent with the ring formulation of the polymeric organic polysulphides (Fuller, *Chem. Reviews*, 1940, **26**, 160).

The precise mechanism of the removal of sulphur from polysulphides by sodium sulphite or sodium hydroxide is not altogether clear, although when the former reagent is used it appears certain that the polysulphide is converted mainly into disulphide (Armstrong, Little, and Doak, *Ind. Eng. Chem.*, 1944, **36**, 628) although a small proportion (not exceeding 10%) of it undergoes reduction to thiols. Probably there is fission of the sulphur chain, giving thio-radicals which recombine to form disulphides, or, to a small extent, are reduced to thiols, while the sulphur liberated converts sodium sulphite into thiosulphate.

Although the thermal decomposition at 170—180° of some polysulphides containing olefinic unsaturation gives thiols and hydrogen sulphide, together with a sulphurated product of much reduced hydrogen content (Farmer and Shipley, Part I), it is now found that the thermal decomposition of a saturated tetrasulphide at somewhat lower temperatures (140—150°) gives only disproportionation products (lower and higher polysulphides), neither thiol nor hydrogen sulphide being formed. Moreover, at temperatures below 120°, the tetrasulphides could generally be distilled unchanged.

Interaction of a polysulphide R·S_x·R with *cyclo*hexene in the temperature range 140—180° gave sulphurated products of the type R·S_y·R′ ($y < x$) in which R was an organic group from the original polysulphide and R′ was *cyclo*hexyl or *cyclo*hexenyl, together with disulphides R_2S_2 derived from the original polysulphide, and *cyclo*hexyl *cyclo*hexenyl di- and poly-sulphides. The latter were similar to the polysulphides resulting from the reaction of sulphur itself with *cyclo*hexene, but contained a smaller sulphur chain. Diethyl tetrasulphide and *cyclo*hexene yielded rather complex mixtures in which the more volatile components could not be adequately separated by distillation, so it was not possible to confirm or to exclude the presence of either the *cyclo*hexanethiol or the *cyclo*hexene episulphide expected from the work of Jones and Reid (*J. Amer. Chem. Soc.*, 1938, **60**, 2452). The presence of some *cyclo*hexyl ethyl sulphide was, however, established beyond doubt by the isolation of cyclo*hexyl ethyl sulphone* on oxidation of the most volatile portion of the reaction product. When polysulphides containing larger organic groups were used, the separation of volatile components was facilitated, although the separation of non-volatile components became correspondingly more difficult. In spite of the most careful search, *cyclo*hexene episulphide could in no case be detected, and the total amount of *cyclo*hexanethiol formed, together with thiols derived from the original polysulphide, was extremely small. The most volatile products in every instance consisted of mixed monosulphides of the type $C_6H_{11}S$·R, R being an organic group of the original tetrasulphide, although when *di*-p-*chlorophenyl tetrasulphide* reacted with *cyclo*hexene some di*cyclo*hexyl sulphide was formed in addition to *p*-chlorophenyl *cyclo*hexyl sulphide. The origin of the di*cyclo*hexyl sulphide in the latter case is obscure.

Unsaturated polysulphides obtained by reaction of sulphur with *cyclo*hexene reacted at 140° with further *cyclo*hexene to give polysulphides with shorter sulphur chains, separable into components none of which appeared to be of greater sulphur chain-length than a tetrasulphide, with an increasing tendency towards saturation in the more volatile components. The amount of material available did not, however, permit of the isolation of a monosulphide.

It is accordingly suggested that the thermal decomposition of polysulphides at temperatures below 180° involves thermal fission of –S–S– bonds. In the absence of a second reactive substance, recombination of fission products regenerates the polysulphides or gives disproportionation products by union of dissimilar fission products. In the presence of an olefin the fission products (or the thiols derived therefrom by hydrogen capture) may either add to the ethylenic linkage, forming, ultimately, a saturated sulphide, or the fission product may link with an allylic radical to form an unsaturated mono-, di-, or poly-sulphide. Simultaneously, reaction occurs between the olefin and sulphur liberated from the sulphur chain of the polysulphide, and since the sulphur may be presumed to be liberated in a rather reactive (possibly atomic) form, the length of the sulphur chain in these products is not large.

It follows that in the reaction of sulphur with olefins, secondary products resulting from the reaction of primarily-formed polysulphides with the olefins are to be expected, especially when the olefin is present in considerable excess. When polysulphides reacted with dihydromyrcene, a considerable quantity of dihydromyrcene cyclic sulphide, identical with that obtained from dihydromyrcene and sulphur (Farmer and Shipley, Part I), was formed. Of particular interest from the point of view of the general reaction of sulphur with polyisoprenes is the ready formation of the cyclic sulphide when dihydromyrcene polysulphide itself was heated with dihydro-

myrcene, and it is hoped soon to ascertain whether the cyclic sulphide formed in the reaction of polyisoprenes with sulphur is a primary product of the olefin–sulphur reaction, or a secondary product formed solely by interaction of polyisoprene polysulphides with the excess of hydrocarbon usually present in these reactions.

Since it is now generally accepted that rubber vulcanisation requires the presence of intermolecular cross-linkages, the combination with rubber of sulphurated fragments of polysulphides alone should not cause vulcanisation unless the sulphurated fragments are themselves polyfunctional (cf. Patrick, U.S.P. 2,235,621). Dialkyl tetrasulphides react fairly readily with rubber, giving *soluble* products containing 2 or 3 units % of combined sulphur which is undoubtedly contained in sulphurated polysulphide fragments added at ethylenic centres of the rubber, since it is well established that products of the reaction of sulphur with rubber, containing considerably less combined sulphur, are quite insoluble. Both the H : C ratio and loss of unsaturation in these tetrasulphide–rubber reaction products are consistent with the postulated incorporation of sulphurated fission products with the rubber; moreover, the product of interaction of di-*p*-chlorophenyl tetrasulphide with rubber contains chemically-combined chlorine as well as sulphur. The insolubility of the latter product is attributed to the presence of sulphur in excess of that resulting from simple addition of sulphurated polysulphide fragments, and it appears certain that some degree of cross-linking has been brought about by the reaction of sulphur itself, liberated from the sulphur chain of the polysulphide. These ideas are consistent with Throdahl and Beavers's observation (*Rubber Chem. Tech.*, 1945, **18**, 110) that, although dialkyl tetrasulphides are incapable of vulcanising rubber, yet some degree of vulcanisation is observed with certain aromatic polysulphides.

It is known that in dehydrogenation reactions at elevated temperatures disulphides are as effective as sulphur itself, the disulphide linkage undergoing cleavage (Ritter and Sharpe, *J. Amer. Chem. Soc.*, 1937, **59**, 2351). If thermal dissociation of disulphides into RS· radicals (cf. Schönberg, *Ber.*, 1933, **66**, 1932) is appreciable at 140°, then it might be expected that disulphides in the presence of sulphur and an olefin would react essentially as polysulphides, and, furthermore, disulphides themselves might be expected to enter into reaction with olefins. Only scanty evidence of the latter type of reactivity has been obtained with disulphides at temperatures below 180°, and diphenyl disulphide, which might be expected to dissociate rather more readily than dialkyl disulphides, proved to be entirely without action on *cyclo*hexene at 180°. Farmer and Shipley have, however, observed the formation of considerable amounts of mercaptobenzthiazole on heating together benzthiazole disulphide and *cyclo*hexene at 140°. Diethyl disulphide and sulphur, heated together at 140—150°, gave no more than trace amounts of polysulphide, and when there was also an olefinic substance present reaction occurred exclusively between the sulphur and the olefin, giving the usual polysulphide products, without any indication of participation of the dialkyl disulphide.

Experimental.

Microanalyses were carried out by Dr. W. T. Chambers, Miss E. Farquhar, and Miss H. Rhodes. Olefinic unsaturation was determined by bromine addition (Bloomfield, *J. Soc. Chem. Ind.*, 1945, **64**, 274).

All the experiments with polysulphides were conducted in sealed glass tubes or glass flasks.

Preparation of Tetrasulphides.—Tetrasulphides were prepared by a modification of the method described by Bezzi (*Gazzetta*, 1935, **65**, 693). A 10% solution of sulphur monochloride (1 mol.) in carbon disulphide was added at room temperature to a 10% solution of the appropriate thiol (2·1 mols.) in the same solvent, and as soon as the initial brisk evolution of hydrogen chloride had subsided the solution was gently boiled for 30 minutes under a reflux condenser. The solvent was then removed at room temperature under reduced pressure, and, with the exception of di-*p*-chlorophenyltetrasulphide, which crystallised from the residue, the residual tetrasulphide was finally distilled.

Properties of Tetrasulphides.—Diethyl (sample A) had b. p. 58—60°/0·1 mm., $n_D^{20°}$ 1·6172; di-*n*-butyl was molecularly distilled at 56° in a falling-film molecular still (Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, **65**, 164) and had $n_D^{20°}$ 1·5772; di*iso*amyl, molecularly distilled at 56°, had $n_D^{20°}$ 1·5542; *di*cyclo*hexyl*, molecularly distilled at 100°, had n_D^{20} 1·6050 (Found: C, 49·0; H, 7·45; S, 43·3. $C_{12}H_{22}S_4$ requires C, 48·95; H, 7·55; S, 43·5%); diphenyl, molecularly distilled at 110°, had $n_D^{20°} > 1·7$; *di*-p-*chlorophenyl*, recrystallised from light petroleum, had m. p. 57° (Found: C, 40·65; H, 2·35; Cl, 20·3; S, 36·25. $C_{12}H_8Cl_2S_4$ requires C, 41·05; H, 2·30; Cl, 20·2; S, 36·5). The author is also indebted to Dr. F. W. Shipley for a sample (B) of diethyl tetrasulphide, b. p. 45°/0·01 mm., $n_D^{19°}$ 1·610, prepared by interaction of ethyl iodide and sodium tetrasulphide. The proportion of the total sulphur content (hereinafter designated " removable sulphur ") removable by a boiling 10% aqueous solution of sodium sulphite was determined for each of these tetrasulphides (Table I).

Thermal Decomposition of Dicyclohexyl Tetrasulphide.—The tetrasulphide (17·1 g.) in purified *cyclo*hexane (50 c.c.) was heated for 4 hrs. at 140°, air being excluded. Molecular distillation of the solvent-free product yielded a relatively small amount (2·9 g.) of material of reduced sulphur content which had $n_D^{20°}$ 1·5816 (Found: C, 53·7; H, 8·35; S, 38·0; removable S, 3 hrs., 25·2, 8 hrs., 31·8%), a considerable amount (9·6 g.) of mainly unchanged di*cyclo*hexyl tetrasulphide, $n_D^{20°}$ 1·6032 (Found: C, 49·75;

TABLE I.

Tetrasulphide.	Removable sulphur, %: 3 hrs. at 100°.	8 hrs. at 100°.
Diethyl (A)	50	50
Diethyl (B)	49	not determined
Di-*n*-butyl	30	45
Di*iso*amyl	44	50
Di*cyclo*hexyl	11	44
Diphenyl	50	52
Di-*p*-chlorophenyl	50	50

H, 7·55; S, 42·3; removable S, 3 hrs., 9·2; 8 hrs., 37·2%), and a relatively small amount (1·7 g.) of viscous *di*cyclo*hexyl hexasulphide*, $n_D^{20°}$ 1·664 (Found: C, 39·8; H, 6·15; S, 53·7; removable S, 3 hrs., 43·2, 8 hrs., 49·2. $C_{12}H_{22}S_6$ requires C, 40·2; H, 6·2; S, 53·6%). The infra-red spectrum of the hexasulphide revealed no unsaturation.

Reaction of Tetrasulphides with Olefins.—(1) *Diethyl tetrasulphide and* cyclo*hexene*. The tetrasulphide (sample A, 20 g.) and *cyclo*hexene (50 c.c.) were heated together for 4 hrs. at 140° in the absence of air. After removal of unchanged *cyclo*hexene (34 g.), the product was separated into a wide range of fractions, b. p. 35—75°/0·1 mm. (total weight 18 g.), leaving a viscous residue (6 g.), care being taken to avoid heating above 130° during the distillation. The recovered *cyclo*hexene contained a trace of ethanethiol, but no carbon disulphide could be detected. Redistillation of the volatile portion of the reaction product gave the following main fractions: (i) b. p. 75—77°/13 mm. (3·5 g.), $n_D^{17°}$ 1·5304 (Found: C, 46·05; H, 8·55; S, 46·0; removable S, 2 hrs., 25·9%); (ii), b. p. 77—79°/13 mm. (2·4 g.), $n_D^{17°}$ 1·5388 (Found: C, 42·35; H, 8·05; S, 48·95; removable S, 2 hrs., 28·8%); (iii) b. p. 79°/13 mm. (1·4 g.), $n_D^{17°}$ 1·5490 (Found: C, 38·4; H, 8·25; S, 53·4; removable S, 2 hrs., 30·5%), and (iv) b. p. 55—75°/0·1 mm. (8·4 g.), $n_D^{17°}$ 1·5970 (Found: C, 34·7; H, 6·4; S, 59·3; removable S, 2 hrs., 47·3%). Further fractionation of fraction (iv) gave sub-fractions of unchanged *n*. Since the H : C ratio of fractions (i), (ii), and (iv) indicated the presence of a considerable proportion of *cyclo*hexyl groups, the most volatile fraction (i) was reduced by sodium in alcohol, whereby di- and poly-sulphides were converted into sodium mercaptides. Oxidation with acid permanganate of the alkali-insoluble components of the reduced product gave cyclo*hexyl ethyl sulphone*, m. p. 34° (Found: C, 54·55; H, 9·30; S, 18·1. $C_8H_{16}O_2S$ requires C, 54·55; H, 9·15; S, 18·2%). The non-volatile portion of the original reaction product contained mainly *cyclo*hexyl and *cyclo*hexenyl groups (Found: C, 38·6; H, 5·7; S, 54·5; removable S, 4 hrs., 51%). Only a trace of *cyclo*hexanethiol was detected in the reaction product, and no *cyclo*hexene episulphide was isolated.

(2) *Diisoamyl tetrasulphide and* cyclo*hexene*. The tetrasulphide (17 g.) and *cyclo*hexene (50 c.c.) were heated together for 4 hrs. at 180° in the absence of air. Distillation of the reaction product yielded (*a*) unchanged *cyclo*hexene (25 c.c.), (*b*) a fraction, b. p. 60—75°/0·01 mm. (21·2 g.), and (*c*) a residue (15·7 g.) not distillable below 100°/0·01 mm. The unchanged *cyclo*hexene was carefully redistilled (Fenske column) and the residue was united with traces of liquid of b. p. <60°/0·01 mm. isolated during the preliminary separation; the combined liquids (0·5 g.), redistilled at 13 mm., consisted entirely of thiols (Found: C, 64·8; H, 10·4; S, 24·8; active H, 0·75% = 24·0% S as ·SH). Fraction (*b*) was redistilled at 0·1 mm., and yielded mainly *cyclo*hexyl *iso*amyl sulphide (12·5 g.), b. p. 58—60°, $n_D^{20°}$ 1·4860 (Found: C, 70·2; H, 11·6; S, 18·2; removable S, nil. Calc. for $C_{11}H_{22}S$: C, 71·0; H, 12·0; S, 17·2%), together with the following fractions of higher sulphur content: (i) b. p. 60—62° (2·7 g.), $n_D^{20°}$ 1·4909 (Found: C, 69·75; H, 11·45; S, 18·75%); (ii) b. p. 62—65° (0·6 g.), $n_D^{20°}$ 1·5018; (iii) b. p. 65—70° (2 g.), $n_D^{20°}$ 1·5142 (Found: C, 68·55; H, 10·7; S, 20·5%), and (iv) b. p. 70—75° (2·2 g.), $n_D^{20°}$ 1·5218 (Found: C, 65·25; H, 10·2; S, 24·4; removable S, 3 hrs., 12%; *M*, 198; I. V., 46). Permanganate oxidation of the bulk fraction of *cyclo*hexyl *iso*amyl sulphide gave the sulphone (yield, 60%), m. p. 57—58° (Found: C, 60·25; H, 10·2; S, 14·7%. Calc. for $C_{11}H_{22}SO_2$: C, 60·5; H, 10·2; S, 14·65%), which had mixed m. p. 57° with an authentic specimen of m. p. 57° (Cunneen, this vol., p. 36). The non-distillable residue (*c*) was passed through the molecular still at 56°, at which temperature about half of the material was volatile. The distillate (6·3 g.), a pale yellow mobile oil, had $n_D^{20°}$ 1·5458, and consisted mainly of disulphides (Found: C, 63·8; H, 9·55; S, 26·85; removable S, 8 hrs., 1·5%; *M*, 215). The brown, rather viscous residue (6·1 g.), $n_D^{20°}$ 1·5818, was of greater molecular complexity (Found: C, 61·35; H, 8·4; S, 30·0; removable S, 8 hrs., 10·7%; *M*, 318). Infra-red examination of both distillate and residue showed the presence of *iso*amyl groups, and also revealed the presence of unsaturation of an apparently conjugated type.

A similar experiment conducted at 140° with 12·7 g. of the tetrasulphide gave no *cyclo*hexene episulphide and no more than a trace of thiols. Some *cyclo*hexyl *iso*amyl sulphide (2·9 g.) was isolated from the crude reaction product; on passing the remainder through the molecular still the volatile portion (7·4 g.), containing considerable unchanged di*iso*amyl tetrasulphide, had $n_D^{20°}$ 1·5481 (Found: C, 48·05; H, 8·55; S, 43·1; removable S, 3 hrs., 37·0; 8 hrs., 43·5%; *M*, 250), but the non-volatile residue (2·1 g.) had $n_D^{20°}$ 1·5958 and probably consisted mainly of *cyclo*hexyl *iso*amyl polysulphide and *cyclo*hexenyl *iso*amyl polysulphide (Found: C, 43·35; H, 7·0; S, 48·3; removable S, 3 hrs., 45·2; 8 hrs., 53·0%; *M*, 312. Calc. for $C_5H_{11}S_{4\cdot6}C_6H_{10\cdot2}$: *M*, 301). The high proportion of removable sulphur after 3 hrs. at 100° indicates the absence of any appreciable amount of di*cyclo*hexyl tetrasulphide. Treatment of the non-volatile residue with further *cyclo*hexene for 3 hrs. at 140° gave an increase in weight of 23%, and pot-still molecular distillation of the product gave two fractions of substantially lower sulphur content than the original material; the distillate had $n_D^{20°}$ 1·5358 (Found: C, 56·7; H, 9·3; S, 33·85; removable S, 3 hrs., 28·7; 8 hrs., 30·7%, corresponding to $C_5H_{11}S_{2\cdot5}C_6H_{10\cdot2}$) and the residue had $n_D^{20°}$ 1·6062 (Found: C, 48·95; H, 7·4; S, 42·8; removable S, 3 hrs., 29·7; 8 hrs., 39·2%, corresponding to $C_5H_{11}S_{3\cdot3}C_6H_{10}$).

(3) *Dicyclohexyl tetrasulphide and* cyclo*hexene*. 9·2 G. of the tetrasulphide, heated for 3 hrs. at

180° with excess of *cyclo*hexene, gave 9 g. of di*cyclo*hexyl sulphide free from unsaturation (Found: C, 72·7; H, 11·2; S, 16·2. Calc. for $C_{12}H_{22}S$: C, 72·7; H, 11·15; S, 16·15%), together with higher sulphides containing unsaturation, *e.g.*, a disulphide (5·8 g.), b. p. >100°/0·01 mm., $n_D^{20°}$ 1·5792 (Found: C, 61·6; H, 8·75; S, 29·3%). Oxidation of the di*cyclo*hexyl sulphide gave di*cyclo*hexyl sulphone, m. p. 132·5°, in 80% yield (Found: C, 62·4; H, 9·7; S, 13·65. Calc. for $C_{12}H_{22}O_2S$: C, 62·55; H, 9·65; S, 13·9%).

(4) *Di-p-chlorophenyl tetrasulphide and* cyclo*hexene*. The product obtained by heating together the tetrasulphide (23·6 g.) and *cyclo*hexene (50 c.c.) was separated by one passage through the molecular still at 56° into a pale yellow distillate (A, 14·8 g.) and a golden brown residue (B, 25 g.) which on a second passage through the still at 80° was further separated into a pale yellow distillate (C, 16·0 g.) and a residue (D, 7·3 g.). The distillate A, which had $n_D^{20°}$ 1·5661 (Found: C, 65·9; H, 7·8; Cl, 11·25; S, 15·05%), was redistilled from a flask at 0·001 mm., giving the following fractions: (i) b. p. 72—80° (0·8 g.), $n_D^{20°}$ 1·5252; (ii) b. p. 80—85° (2·0 g.), $n_D^{20°}$ 1·5342 (Found: C, 70·75; H, 9·95; Cl, 3·9; S, 15·3. Calc. for 24·6% $C_{12}H_{15}ClS$ + 73·4% $C_{12}H_{22}S$: C, 69·0; H, 9·80; Cl, 3·9; S, 15·3%), (iii) b. p. 85—92° (2·7 g.), $n_D^{20°}$ 1·5541 (Found: C, 68·45; H, 8·7; Cl, 7·9; S, 15·05. Calc. for 50·5% $C_{12}H_{15}ClS$ + 49·5% $C_{12}H_{22}S$: C, 68·05; H, 8·9; Cl, 7·9; S, 15·1%), (iv) b. p. 92—96° (4·1 g.), $n_D^{20°}$ 1·5762 (Found: C, 65·3; H, 7·05; Cl, 13·95; S, 14·4. Calc. for 89·2% $C_{12}H_{15}ClS$ + 10·8% $C_{12}H_{22}S$: C, 64·5; H, 7·1; Cl, 13·95; S, 14·3%), and a liquid residue (v), not distillable without overheating, $n_D^{20°}$ 1·5808, from which crystallised p-*chlorophenyl* cyclo*hexyl sulphide*, m. p. 25° (Found: C, 63·85; H, 6·8; Cl, 15·75; S, 14·05. $C_{12}H_{15}ClS$ requires C, 63·55; H, 6·7; Cl, 15·65; S, 14·1%). Oxidation of fraction (iv) gave a 62% yield of p-*chlorophenyl* cyclo*hexyl sulphone*, m. p. 68—69° (Found: C, 55·9; H, 5·85; Cl, 13·95; S, 12·4. $C_{12}H_{15}O_2ClS$ requires C, 55·7; H, 5·85; Cl, 13·7; S, 12·4%).

(5) cyclo*Hexyl* cyclo*hexenyl polysulphide and* cyclo*hexene*. A typical polysulphide (Found: C, 34·55; H, 4·85; S, 59·6%), obtained by the action of sulphur on *cyclo*hexene, was heated with an excess of *cyclo*hexene for 3 hrs. at 140°. There was a weight increase of 14% and the product yielded a distillate (pot still) which had $n_D^{20°}$ 1·5805 (Found: C, 56·1; H, 8·1; S, 36·15; removable S, 8 hrs., 33·2%) and a residue which had $n_D^{20°}$ 1·6260 (Found: C, 51·0; H, 7·0; S, 40·9; removable S, 8 hrs., 29·6%).

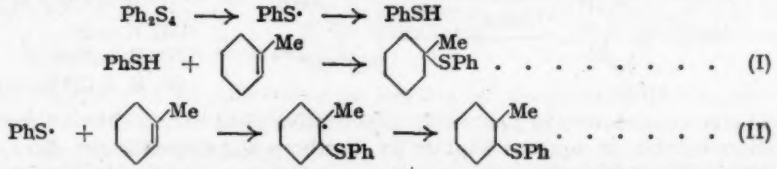
(6) *Diphenyl tetrasulphide and dihydromyrcene*. The tetrasulphide (19·1 g.) and dihydromyrcene (50 c.c.), heated together for 3 hrs. at 150° in the absence of air, yielded dihydromyrcene cyclic sulphide (3·8 g.) and a reddish-brown oil (29·7 g.) which was separated by passage through the molecular still at 80° into a volatile red liquid (21·7 g.) (Found: C, 72·4; H, 7·9; S, 18·7%) which deposited considerable diphenyl disulphide, and a brown viscous residue (4·0 g.) (Found: C, 61·85; H, 7·45; S, 31·7%).

(7) *Dihydromyrcene polysulphide and dihydromyrcene*. The polysulphide (5·5 g.), obtained by the action of sulphur on dihydromyrcene, and freed from cyclic sulphide and free sulphur by repeated passage through the molecular still, was heated with dihydromyrcene (20 c.c.) for 3 hrs. at 145° and yielded 3·3 g. of dihydromyrcene cyclic sulphide together with 6·5 g. of non-volatile matter (Found: C, 57·35; H, 8·6; S, 33·35%).

(8) *Tetrasulphides and rubber*. The tetrasulphides were incorporated into the rubber by milling, the mixtures were heated in sealed evacuated tubes for 3 hrs. at 140°, and the products were extracted with acetone and with chloroform if they were sufficiently insoluble. Diethyl tetrasulphide (0·76 g.) and rubber (5 g.) yielded a reddish-brown product (Found: C, 84·8; H, 11·65; S, 2·8%; I.V., 328) which was soluble in benzene and in chloroform. Di-*p*-chlorophenyl tetrasulphide (1·1 g.) and rubber (4 g.) yielded an insoluble product (Found: C, 79·1; H, 10·45; Cl, 2·65; S, 7·25%).

This paper forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The author expresses his thanks to Dr. E. H. Farmer for his advice and criticism, and to Mr. N. Sheppard for infra-red examination of some of the polysulphides.

Note added in Proof.—Since the above papers were submitted the reaction mechanism involved in the formation of saturated monosulphides by the interaction of polysulphides with olefins has been clarified by a study of the reaction of diphenyl tetrasulphide with 1-methyl-*cyclo*hexene. Since the major reaction product is phenyl 1-methyl*cyclo*hexyl sulphide and not phenyl 2-methyl*cyclo*hexyl sulphide it appears certain that the reaction involves hydrogen-capture by the fission product of the polysulphide and addition of the resulting thiol to the double bond by a polar mechanism (I) rather than by a radical addition of the fission product to the double bond followed by hydrogen-capture at the other ethylenic carbon atom (II).



The structure of the sulphide formed was confirmed by mixed m. p. (76°) of the corresponding sulphone with the phenyl 1-methyl*cyclo*hexyl sulphone of m. p. 76° described by Cunneen (*loc. cit.*).

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303. *Derivatives of 6-Methoxyquinaldine with Basic Substituents in the 4-Position.*

By James Walker.

Attention is directed to the smooth replacement of the sulphonic acid group in quinoline-4-sulphonic acids by reaction with amines as a means of preparing quinolines substituted in the 4-position by basic groups.

In contrast with the activity shown by certain 4-dialkylaminoalkylamino-6-methoxyquinolines in bird malaria (Magidson and Rubtsov, *J. Gen. Chem. Russia*, 1937, **7**, 1896), no activity was observed in analogous quinaldines (*e.g.*, Kermack and Smith, *J.*, 1931, 3096; Krichevskii *et al.*, *J. Microbiol. Epidemiol. Immunobiol. Russia*, 1935, **14**, 642). In view of the greater accessibility of the quinaldines as compared with the quinolines of this type, the present author, towards the end of 1941, began a further investigation of other 6-methoxyquinaldines, but, while the work was still in progress, essentially the same project was independently covered by Holcomb and Hamilton (*J. Amer. Chem. Soc.*, 1942, **64**, 1309), who actually record the observation of antimalarial activity in 4-γ-diethylaminopropylamino-6-methoxyquinaldine (I), and the writer's interest was then withdrawn from this topic although the work, as now described below, differed in technical detail from that of Holcomb and Hamilton. In the interval, however, much attention has been devoted to the subject of quinolines substituted in the 4-position by basic side-chains in view of the marked antimalarial properties of resochin (7-chloro-4-δ-diethylamino-α-methylbutylaminoquinoline), which can be regarded as being derived from mepacrine by ablation of the methoxylated benzene ring, and the corresponding 3-methyl compound, sontochin (D.R.-P. 683,692; U.S.P. 2,233,970). Much has recently been published in the United States in this connection (*e.g.*, Drake *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 1208, 1214; Tarbell *et al.*, *ibid.*, p. 1217; Carmack *et al.*, *ibid.*, p. 1220; Pearson, Jones, and Cope, *ibid.*, p. 1225; Riegel *et al.*, *ibid.*, p. 1229; Breslow *et al.*, *ibid.*, p. 1232; Elderfield *et al.*, *ibid.*, p. 1250). The method regularly used for the introduction of the aliphatic basic side-chains into the 4-position of quinolines has been to condense the appropriate 4-chloro-compounds with the appropriate amines at a high temperature, and fair yields have been reported as a rule. Occasionally, phenol has been added as a catalyst but it does not appear to have the same marked influence in the quinoline series as it has with 5-chloroacridines (cf. Magidson and Grigorowsky, *Ber.*, 1936, **69**, 400). Potassium iodide has also been applied as a catalyst but there is little evidence of its efficaciousness, and glacial acetic acid has been used as a solvent in such condensations with aliphatic amines (Meyer and Drutel, *Compt. rend.*, 1936, **205**, 148) although its use is more familiar with anilines (*e.g.*, Fischer, Diepolder, and Wölfel, *J. pr. Chem.*, 1925, **109**, 59).

The present paper records the use of *6-methoxyquinaldine-4-sulphonic acid* (II) for this purpose in an application of a method outlined in the patent literature (D.R.-P. 615,184). In the original patent, quinoline-2- or -4-sulphonic acids were condensed with amines with or without the addition of a catalyst, such as zinc chloride, but the latter was used in the experiments described below, in which (II) has been condensed with ammonia to give 4-amino-6-methoxyquinaldine (III), with α-aminopyridine to give *4-α-pyridylamino-6-methoxyquinaldine* (IV) in poor yield, with γ-diethylaminopropylamine to give (I) (characterised as the dihydrochloride), and with δ-diethylamino-α-methylbutylamine to give *4-δ-diethylamino-α-methylbutylamino-6-methoxyquinaldine* (V) (characterised as the *dihydrobromide*). The sulphonic

(II.)

(I) R = $CH_2 \cdot CH_2 \cdot CH_2 \cdot NEt_2$
(III) R = H
(IV) R = C_5H_4N
(V) R = $CHMe \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NEt_2$

acid (II) was obtained in practically quantitative yield from 4-chloro-6-methoxyquinaldine and sodium sulphite in aqueous solution (cf. Besthorn and Geisselbrecht, *Ber.*, 1920, **53**, 1017), and subsequent condensation with amines proceeded as a smooth homogeneous reaction affording products which readily crystallised in the crude state (cf. Bachman and Cooper, *J. Org. Chem.*, 1944, **9**, 307). Holcomb and Hamilton (*loc. cit.*) failed to isolate a satisfactory condensation product from 4-chloro-6-methoxyquinaldine and α-aminopyridine, but a small yield of the expected product was readily isolated using the sulphonic acid. Furthermore, condensation with ammonia proceeded particularly readily with the sulphonic acid in marked contrast with

the behaviour of 4-chloroquinolines (cf. Elderfield *et al.*, *loc. cit.*; Backeberg and Marais, *J.*, 1942, 381).

Tests for therapeutic activity in *P. relictum* infections in canaries were kindly carried out by Dr. Ann Bishop at the Molteno Institute, Cambridge, on sodium 6-methoxyquinaldine-4-sulphonate, 4-α-pyridylamino-6-methoxyquinaldine (IV), and 4-δ-diethylamino-α-methylbutylamino-6-methoxyquinaldine (V) dihydrobromide, but no activity was detected. It is now obvious that a methyl group in the 2-position in quinolines, though not in the 3-position (cf. sontochin), has a marked dystherapeutic effect probably by presenting to the host a point of metabolic attack.

Experimental.

6-Methoxyquinaldine-4-sulphonic Acid (II).—Ethyl *β-p*-anisidinocrotonate (Coffey, Thomson, and Wilson, *J.*, 1936, 856) was cyclised by Limpach's technique (*Ber.*, 1931, **64**, 969) and the resulting 4-hydroxy-6-methoxyquinaldine was converted into the chloro-compound in 90% yield following the method of Fischer *et al.* (*loc. cit.*). 4-Chloro-6-methoxyquinaldine (5 g.) was refluxed with an aqueous solution (40 c.c., adjusted to pH 8 with N-hydrochloric acid) of sodium sulphite heptahydrate (12 g.) until a homogeneous solution was obtained (3½ hours) and then for a further ½ hour. The solution, treated with norite, was filtered and cooled, affording a copious separation of colourless prisms of the sodium salt The free *acid*, precipitated by acidifying an aqueous solution of the sodium salt to Congo-red with 16% hydrochloric acid, separated from water in pale cream-coloured hydrated prisms which lost part of the water of crystallisation in a vacuum desiccator, darkened at about 296°, and had m. p. 302—303° (decomp.) (Found: C, 48·6; H, 5·0; N, 5·2. $C_{11}H_{11}O_4NS,H_2O$ requires C, 48·7; H, 4·8; N, 5·2%). The yield was nearly quantitative.

4-Amino-6-methoxyquinaldine (III).—6-Methoxyquinaldine-4-sulphonic acid (6 g.), 25% aqueous ammonia solution (30 c.c.), and zinc chloride (1 g.) were heated in a sealed tube at 130° for 20 hours. On cooling, large yellow plates were deposited. The mixture was warmed to effect solution, cooled, and treated with excess of 2N-sodium hydroxide (25—30 c.c.). The precipitated oil rapidly crystallised in colourless needles (3·75 g.; 84%), m. p. 206°. Recrystallisation from dilute aqueous alcohol afforded thin plates, m. p. 208—209° (Found: C, 70·0; H, 6·5; N, 14·9. Calc. for $C_{11}H_{12}ON_2$: C, 70·2; H, 6·4; N, 14·9%). Koenigs and v. Loesch (*J. pr. Chem.*, 1935, **143**, 59) record m. p. 211—213°, and Backeberg and Marais (*loc. cit.*) record m. p. 209°.

4-α-Pyridylamino-6-methoxyquinaldine (IV).—6-Methoxyquinaldine-4-sulphonic acid (5·06 g.), freshly distilled α-aminopyridine (3·8 g.), zinc chloride (1 g.), and water (25 c.c.) were heated in a sealed tube at 140° for 30 hours. The product was distributed between ether and excess of 2N-sodium hydroxide. The ether was well washed with water, dried, and evaporated, affording a cream-coloured *solid* (0·33 g.; 6·2%), which separated from benzene in rosettes of fine colourless prisms, m. p. 196—197° (Found: C, 72·6; H, 5·7; N, 15·5. $C_{16}H_{15}ON_3$ requires C, 72·5; H, 5·7; N, 15·8%).

4-γ-Diethylaminopropylamino-6-methoxyquinaldine (I) *Dihydrochloride.*—6-Methoxyquinaldine-4-sulphonic acid (5·06 g.), γ-diethylaminopropylamine (4·3 g.), zinc chloride (1·2 g.), and water (18 c.c.) were heated in a sealed tube at 140° for 24 hours. The product was distributed between ether and 3N-sodium hydroxide. The ethereal solution was well washed with water, dried, and evaporated, affording a stiff pale yellow syrup which crystallised completely in the form of transparent plates (4·26 g.; 71%); the solid did not remelt on the boiling water-bath. The base was dissolved in a small volume of warm alcohol and treated with the calculated volume of alcoholic hydrochloric acid. The dihydrochloride, obtained on evaporation, separated from ethyl alcohol–ethyl acetate (1 : <1) in minute clusters of colourless prisms, m. p. 134° (Found, in material dried over sulphuric acid in a vacuum: C, 53·7, 54·2; H, 7·9, 7·8; N, 10·5. $C_{18}H_{27}ON_3,2HCl,1\frac{1}{2}H_2O$ requires C, 53·9; H, 8·0; N, 10·5. Calc. for $C_{18}H_{27}ON_3,2HCl,2H_2O$: C, 52·7; H, 8·0; N, 10·2%). Holcomb and Hamilton (*loc. cit.*) obtained a dihydrate, and record m. p. 126—127°; Van Arendonk and Shonle (*J. Amer. Chem. Soc.*, 1944, **66**, 1284) record m. p. 125—126°.

4-δ-Diethylamino-α-methylbutylamino-6-methoxyquinaldine (V) *Dihydrobromide.*—6-Methoxyquinaldine-4-sulphonic acid (7·6 g.), δ-diethylamino-α-methylbutylamine (9·6 g.), zinc chloride (1 g.), and water (20 c.c.) were heated in a sealed tube at 150° for 20 hours. The product was isolated as in the preceding case and the *base*, obtained initially as an amber syrup (6·6 g.; 67%), rapidly crystallised, affording a cream-coloured solid, m. p. 120—122°, clearing at 123° (Found: OMe, 9·5. $C_{20}H_{31}ON_3$ requires OMe, 9·4%). The *dihydrobromide*, obtained by neutralisation with the calculated volume of N-hydrobromic acid and evaporation to dryness, separated from ethyl alcohol–ethyl acetate (approx. 1 : 2) in clusters of colourless radiating prisms, m. p. 197—198° (Found: C, 48·7; H, 6·7; N, 8·4; Br, 32·3. $C_{20}H_{31}ON_3,2HBr$ requires C, 48·9; H, 6·7; N, 8·6; Br, 32·6%). The dihydrochloride of this base has been described by Holcomb and Hamilton (*loc. cit.*).

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304. *Strychnine and Brucine. Part XLVII. Oxodihydroneostrychnine and Oxodihydromethoxymethyldihydroneostrychnine.*

By R. N. Chakravarti, K. H. Pausacker, and Sir Robert Robinson.

It is shown that bases of the *neo*-series are characterised by facile oxidation to oxo-derivatives formed by addition of one atom of oxygen. The carbon–nitrogen skeleton of strychnine is found unaltered in reduction products of these substances.

In the course of attempts to prepare the methiodide of methoxymethyldihydro*neo*strychnidine in methanolic solution it was found that oxidation occurred and the product was termed oxymethoxymethyldihydro*neo*strychnidine-A, m. p. 235°. It was convertible into an isomeride-B, m. p. 280° (285°), in various ways, for example by boiling with xylene or acetone (Clemo, Perkin, and Robinson, *J.*, 1927, 1608). No semicarbazone could be prepared, and the base was unchanged by boiling acetic anhydride. It was recognised that the methyl iodide was a source of a trace of catalytic iodine, and the brucidine analogue was obtained by the use of methanol and a crystal of iodine (Gulland, Perkin, and Robinson, *J.*, 1927, 1643).

In a later paper (Achmatowicz, Perkin, and Robinson, *J.*, 1932, 495), the oxidation of methoxymethyldihydro*neo*strychnidine by means of potassium permanganate in acetone solution was studied. The product was an acetone compound of the oxymethoxydihydro*neo*strychnidine-C, m.p. 305—306°. The opinion was expressed that (C) is (B) in purer form.

An interesting observation was the conversion of the isomeride-C into oxymethyl*neo*strychnidinium salts by boiling it with 20% sulphuric acid. The iodide was analysed, and the related chloride could be converted into the base-C by the action of methanolic potassium hydroxide. This was regarded as a proof that the oxygen taken up is not present in a labile group such as an ethylene oxide.

Our further observations suggest that these so-called isomerides are either very labile isomerides or owe their differing melting points to the presence of tenaciously held solvent.

Material of m. p. 285°, corresponding to isomeride-B, afforded a p-*nitrophenylhydrazone* which could not, however, be fully purified by crystallisation. It gave the characteristic colour reaction of its class with aqueous alcoholic sodium hydroxide.

The bases of m. p. 210—224° (A) and m. p. 285° (B) were converted in the known manner in oxy*neo*strychnidine methiodide; the same product was obtained in each case and it tallied with the description (*loc. cit.*) of the salt from isomeride-C. On treatment with methanolic potassium hydroxide the latter base was produced.

An indication that the skeleton was unaltered by the oxidation was afforded by reduction of isomeride-B under Clemmensen's conditions with formation of methoxymethyltetrahydrostrychnidine. These results suggest that the oxidation product is an aldehyde or ketone, and we propose the replacement of the prefix "oxy" by "oxodihydro". Methoxymethyldihydro*neo*strychnine is found to be convertible into *oxodihydromethoxymethyldihydroneostrychnine* either by leaving a methanolic solution containing a trace of iodine to evaporate in the air, or by boiling with methanol and methyl iodide. The use of ethanol led to the formation of an uncrystallisable gum. The new base holds firmly ½ MeOH or ½ EtOH. Although it certainly forms a *p*-nitrophenylhydrazone, this derivative showed no tendency to crystallise. The base was also oxidised by means of ferric chloride in N-hydrochloric acid. The crystalline product appears to have the composition $C_{46}H_{56}O_7N_4$, that is, two molecules of the base take up one atom of oxygen. A low value was obtained for the molecular weight in fused camphor, but this is probably due to fission of the molecule under the conditions of the experiment. A very satisfactory oxidation of *neo*strychnine occurs when its acid solution is treated with bromine water in the cold. The *hydrobromide* of *oxodihydroneostrychnine* * crystallises in high yield. The free *base* exhibits interesting properties and transformations which will be described in detail in a subsequent communication. It is mentioned here because the composition change is the same as that observed in other cases and because this substance is the most characteristic of the oxodihydro*neo*-bases which we have encountered.

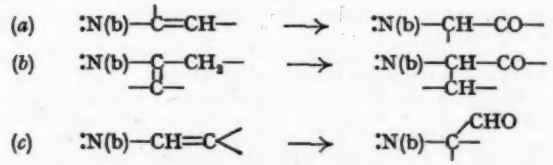
Although this and the other oxodihydro-bases reduce ammoniacal silver solutions with ease and slowly reduce Fehling's solution, it does not follow that they are aldehydes. It is well known that many α-amino-ketones are readily oxidised by the reagents mentioned.

The aldehyde hypothesis seems to be inconsistent with the reduction of oxodihydromethoxy-

* The use of *neo* in this name may be superfluous because dihydro*neo*strychnine is dihydrostrychnine. But this depends on the validity of our views and the *neo* is retained in order to show the origin of the base.

methyl*neo*strychnidine to methoxymethyltetrahydrostrychnidine and with the formation of oxodihydromethoxymethylstrychnidine-C from oxodihydromethylstrychnidinum salts by the action of such a vigorous reagent as methyl alcoholic potassium hydroxide.

The only rational explanations of the formation of these oxodihydro*neo*-bases that we can devise are as follows:



Added May 9th, 1947.—It now seems probable that oxodihydro*neo*strychnidine is not analogous to the other oxo-compounds mentioned herein, and the discussion is therefore postponed.

Added November 9th, 1947.—It has been established that the salt first formed is a *neo*strychnine dibromide (one bromidion) which changes to oxodihydro*allo*strychnine hydrobromide in warm aqueous solution. The free base is an aldehyde produced in accordance with hypothesis (*c*). A statement of these relations was made to the Organic Chemistry Section of the International Congress of Chemistry (London, 1947).

Experimental.

Oxodihydromethoxymethyldihydroneostrychnidine.—This substance was obtained by the known method (*loc. cit.*, 1927) and had variable m. ps. ranging from 210° to 224° (lit. 235°) in different runs. After addition of methanol to a solution in pyridine, the crystals that separated had m. p. 285° and the same value was reached by refluxing the initial product with ethanol or acetone. Only a small quantity of dark material remained in the filtrate.

Oxidation of methoxymethyldihydro*neo*strychnidine (7 g.) by means of potassium permanganate in acetone solution (*loc. cit.*, 1932) gave 0·5 g. of the variety, m. p. 305°. This separated on concentration of the acetone solution, and the bulk of the product was obtained on removal of the solvent as an uncrystallisable oil. It is very difficult to determine whether the varieties, m. p. 285° and m. p. 305°, are identical or not. The mixed m. p. was 288—294°, and when a pyridine solution of the base, m. p. 285°, was mixed with methanol containing a few crystals of the base, m. p. 305°, the separated crystals had m. p. 304—306°. On the other hand the variety, m. p. 285°, can be recrystallised without change of m. p. and no change of m. p. was observed on refluxing it with acetone, alone or in presence of a little sodium hydroxide. Conversion of any of the supposed isomerides into oxymethyl*neo*strychnidine methiodide (*loc. cit.*) gave one and the same salt, m. p. 232—234° (lit., 238—240°) showing undepressed mixed m. ps.

The quaternary chloride from the variety, m. p. 285°, was treated with methanolic potassium hydroxide in the known manner and afforded a base, m. p. 298—300°, m. p. 300—302° on admixture with the variety, m. p. 305°.

A mixture of the variety, m. p. 285° (0·1 g.), *p*-nitrophenylhydrazine (0·04 g.), and acetic acid (2 c.c.) was heated on the steam-bath for ½ hour. Addition of aqueous ammonia precipitated a light yellow amorphous solid which was purified by solution in hot ethanol and addition of water; it could not be crystallised (Found: C, 67·9; H, 7·0. $C_{29}H_{33}O_4N_5$ requires C, 67·3; H, 6·8%). The *substance* softened at 120° and decomposed at 185—186° but these figures have little significance. Its alcoholic solution developed an intense red coloration on the addition of a drop of 10% aqueous sodium hydroxide, the reaction characteristic of *p*-nitrophenylhydrazones. Its acid solution developed a carmine coloration (strychnidine reaction) on addition of ferric chloride. The variety, m. p. 305°, gave a similar *p*-nitrophenylhydrazone exhibiting these reactions.

A mixture of the variety, m. p. 285° (2·0 g.), concentrated hydrochloric acid (5 c.c.), water (4 c.c.), and amalgamated zinc (5 g., prepared according to "Organic Reactions," **1**, 163) was refluxed for 12 hours with the addition of further concentrated hydrochloric acid (1 c.c.) each hour. The diluted solution was basified with sodium hydroxide and the product obtained as a white solid (1·8 g., m. p. 220—221°). The substance was crystallised from benzene and from pyridine–methanol and identified as methoxymethyltetrahydrostrychnidine by observation of the m. p. 220—221°, undepressed on admixture with an authentic specimen.

Oxodihydromethoxymethyldihydroneostrychnine.—Methoxymethyldihydro*neo*strychnine was prepared from methylstrychnine by the method of Achmatowicz, Clemo, Perkin, and Robinson (*J.*, 1932, 769), and a consistent yield of about 75% was secured by a modification of procedure of isolation. After the removal of methanol and addition of water the alkaline solution was mixed with crushed ice and gradually acidified by acetic acid in a funnel with shaking with ether. In this way the formation of gummy by-product was avoided.

(A). Methoxymethyldihydro*neo*strychnine (5 g.) was dissolved in hot methanol (300 c.c.) and a small crystal of iodine added. The solution was allowed to evaporate in the air for a week. Gum was separated from the sparingly soluble crystalline crust by treatment with hot methanol, the solid was collected, and the filtrate allowed to evaporate again. By repetition of this process the yield was 1·8 g. The substance separated from pyridine–methanol as a jelly which became crystalline on warming. It is sparingly soluble in ethanol, and when the solutions were quickly cooled a gel was also formed; on slow cooling, however, the substance separated as radiating cluster of fine needles, which shrank at 225°,

m. p. 275—277° on slow heating. If heated rapidly the m. p. ranges from 230° to 240° (Found in material dried over sulphuric acid : C, 68·6; H, 7·1; N, 6·7; MeO, 11·3. $C_{23}H_{28}O_4N_2$,0·5EtOH requires C, 68·7; H, 7·4; N, 6·7%; 1 MeO + 0·5 EtO, Calc. as MeO, 11·1%). When ethanol was employed in this preparation no crystallisable product was obtained. The *base* dissolves slowly but completely in N-hydrochloric acid and is precipitated by the addition of sodium acetate. It forms a *p*-nitrophenylhydrazone and a 2 : 4-dinitrophenylsemicarbazone, but neither of these derivatives could be crystallised. The former gave an intense orange-red coloration, blue-tinged in thin layers, on the addition of potassium hydroxide to its alcoholic solution.

(B). Methoxymethyldihydro*neo*strychnine (4 g.) was refluxed with methyl iodide (5 c.c.) and methanol (40 c.c.) for 3 hours and then shaken in contact with air for 10 days. The separated crystals (0·6 g.) were deposited from pyridine solution by the addition of methanol as a jelly which crystallised on keeping. This *specimen* softened at 222°, m. p. 275—277° (Found : C, 68·5; H, 6·9. $C_{23}H_{28}O_4N_2$,0·5MeOH requires C, 68·4; H, 7·3%). Recrystallised from ethanol (gel ⟶ crystals) it was obtained in needles, softening at 240°, m. p. 275—277°, and mixed with the product from (A) it softened at 235°, m. p. 275—277°. It is quite possible that the half molecule of solvent is in combination in the form —Ċ(OR)—O—Ċ(OH)— and that the variations of softening points are due to incomplete exchange of R by R′. When iodine (0·2 g.) was used in place of methyl iodide in this procedure, the yield was 1·0 g. The *p*-nitrophenylhydrazone shrank at 130°, m. p. 155—157° (decomp.). Strychnine and methoxymethyldihydro*neo*strychnine immediately decolorise permanganate in very dilute sulphuric acid solution. Oxodihydromethoxymethyldihydro*neo*strychnine is very slowly attacked under these conditions.

Reduction according to Clemmensen afforded a base, m. p. 261—262°, readily soluble in methanol, but the investigation of this substance has not yet been completed.

Oxidation of *Methoxymethyldihydroneostrychnine by Means* of *Ferric Chloride.*—A cold solution of ferric chloride (3·3 g., anhydrous) in water (15 c.c.) was added to one of methoxymethyldihydro*neo*strychnine (3·8 g.) in N-hydrochloric acid (35 c.c.). After an hour the red solution was basified with ammonia, precipitating the base along with ferrous hydroxide. The whole was shaken with ethyl acetate (about 50 c.c.), filtered, and the ester layer separated and evaporated (2·6 g. of crystalline residue). The *substance* is very sparingly soluble in hot methanol or ethanol, readily soluble in dilute hydrochloric acid. It crystallises from chloroform on the addition of ether in small, flat needles, m. p. 190° [Found : C, 70·9; H, 7·1; N, 7·3; *M* (Rast in camphor), 467. $C_{46}H_{56}O_7N_4$ requires C, 71·1; H, 7·2; N, 7·2%; *M*, 776]. The composition suggests a compound of oxodihydromethoxymethyldihydro*neo*strychnine, $C_{23}H_{28}O_4N_2$, and methoxymethyldihydro*neo*strychnine, $C_{23}H_{28}O_3N_2$, but the substance does not afford a *p*-nitrophenylhydrazone and it gives no precipitate on the addition of *p*-nitrobenzenediazonium chloride to an acid solution. Possibly it is an ether, and the composition $C_{46}H_{54}O_7N_4$ (Calc : C, 71·3; H, 7·0; N,7·2%) is not excluded.

Oxodihydroneostrychnine.—A hot solution of *neo*strychnine (8·35 g.) in 1·5N-sulphuric acid (110 c.c.) was cooled to the room temperature and 0·2N-bromine water (250 c.c.) added in 4 to 5 portions with shaking, so that the yellow perbromide that separated was quickly decomposed. The white crystalline precipitate was collected after 15 minutes, washed with a little water, and dried in a vacuum desiccator (9·8 g.). The salt is a *hydrobromide* free from sulphate. Although very sparingly soluble in cold water, it dissolves readily on heating and forms supersaturated solutions. Crystallisation is best effected from concentrated solutions and seeding is necessary. The colourless, well-shaped prisms become deep red with shrinkage at 170° and gradually decompose on further heating (Found : C, 55·2, 56·0; H, 5·6, 5·7; Br, 17·3, 18·7. $C_{21}H_{23}O_3N_2$,HBr,H_2O requires C, 56·1; H, 5·6; Br, 17·8%). The free base was obtained as a chalky precipitate on addition of ammonia to a cold solution of the hydrobromide. It was collected, washed, and dried in a vacuum (7·5 g., m. p. 80—140°). This *product* was dissolved in methanol (80 c.c.) and the solution concentrated to 15—20 c.c. when it separated in stellate clusters of transparent prisms (6 g.), m. p. 128° (decomp.) (Found : C, 69·1; H, 6·9; N, 7·4. $C_{21}H_{22}O_3N_2$,MeOH requires C, 69·1; H, 6·8; N, 7·3%). The solvent is lost slowly at 100°, more rapidly at near 120° (loss, 7·6. Calc. : 8·3%). The solvent-free *base* has m. p. 190° and is hygroscopic (Found : C, 71·6; H, 6·4; N, 7·9. $C_{21}H_{22}O_3N_2$ requires C, 72·0; H, 6·3; N, 8·0%).

It is of interest that oxodihydro*neo*strychnine can also be obtained, although in poor yield, by aerial oxidation of *neo*strychnine in methanol containing iodine. A mixture of *neo*strychnine (3 g.), methanol (120 c.c.), and iodine (0·2 g.) was shaken for 9 days under air. Some *neo*strychnine remained undissolved (1·8 g., m. p. 224—225°) and the filtrate was evaporated and the residue extracted with dilute sulphuric acid. Ammonia precipitated a white solid (0·5 g., m. p. 110° with frothing) and this was converted into the semicarbazone hydrochloride in the usual manner. The salt, when slowly heated, darkened at 240° and decomposed at 255°, and the behaviour was unchanged on admixture with the derivative prepared from oxodihydro*neo*strychnine. The base is sparingly soluble in the simple alcohols but has a tendency to form supersaturated solutions. It is readily soluble in chloroform and can easily be crystallised by addition of ether to a concentrated solution. It is fairly soluble in dilute hydrochloric acid. A silver mirror is formed with ammoniacal silver nitrate after heating on the steam-bath for 10 minutes, and the base also reduces silver oxide in boiling alcoholic suspension, forming a mirror. It slowly reduces Fehling's solution on heating. The Otto reaction (60% sulphuric acid) is a transient violet coloration changing to deep red and finally brown. The *p*-nitrophenylhydrazone is a yellow solid, the alcoholic solution of which becomes deep red on the addition of aqueous sodium hydroxide. Crystalline derivatives showing the presence of a carbonyl group have been prepared and analysed, but a description of these is reserved for a future communication.

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305. *Strychnine and Brucine. Part XLVIII. Degradation of the Strychnineacetic Acid prepared from Pseudostrychnine.*

By K. H. Pausacker and Sir Robert Robinson.

The alkaline degradation of strychnineacetic acid has been studied in the hope of supplying evidence in favour of one of the two structures discussed in Part XLII (Briggs, Openshaw, and Robinson, *J.*, 1946, 903). One of the products should be 3- or 4-methylcarbazole, and an unequivocal result would have been of great value. Actually the main constituent of the carbazole fraction was carbazole itself, but infra-red absorption analysis, carried out by Mr. R. E. Richards of the Physical Chemistry Laboratory, Oxford University, showed that 3-methylcarbazole, but no 4-methylcarbazole, was present in small relative amount.

The carbazole from strychnine was found to contain a trace of 3-methylcarbazole, and degradation of the product of interaction of oxodihydro*neo*strychnine and methylmagnesium iodide afforded a carbazole fraction containing 3-methylcarbazole and an unidentified substance.

For the study of the infra-red absorption 1-, 2-, and 3-methylcarbazoles were prepared by known methods.

4-Methylcarbazole does not appear to have been hitherto described and was synthesised without ambiguity from 4-chloro-*m*-tolylhydrazine by way of a related tetrahydrocarbazole.

Carbazole was first obtained from strychnine by dry distillation and by heating with zinc dust (Lobisch and Schoop, *Monatsh.*, 1886, **7**, 614); by heating strychnine with soda-lime, Lobisch and Malfatti (*ibid.*, 1888, **9**, 626) obtained carbazole, skatole, and β-picoline. The formation of carbazole was confirmed by Clemo, Perkin, and Robinson (*J.*, 1927, 1625), who decomposed methylstrychnine at 150—200°. Such drastic degradations affording aromatic compounds of high intrinsic stability are admittedly of problematic value in constitutional studies, but it occurred to us that the survival of a group introduced into the strychnine molecule would be significant.

It is known that pseudostrychnine (hydroxystrychnine) contains :N(b)·C(OH): (Blount and Robinson, *J.*, 1932, 2305), and Leuchs (*Ber.*, 1943, **76**, 1068) showed that this base condenses with malonic acid to strychnineacetic acid, :N(b)·C·CH_2·CO_2H, which loses carbon dioxide with formation of methylstrychnine.

Degradation of a crude product obtained in this way gave a carbazole fraction which on examination by the usual methods was found to contain methylcarbazoles in considerable relative amount (up to 40%). At this point we were fortunate to receive the valuable co-operation of Mr. R. E. Richards to whom we express our gratitude. He examined the infra-red spectra of carbazole and the four *C*-methylcarbazoles and noted the presence of certain characteristic bands. He also studied our degradation products and synthetic mixtures of carbazole and the various isomerides. The degradation product was found to contain from 5 to 12% of 3-methylcarbazole, and 4-methylcarbazole was absent.

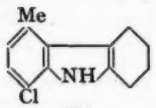
As a control we degraded strychnine by the same method, and the infra-red analysis of the product showed that it was carbazole containing a little (<1%) 3-methylcarbazole. As the 3-position is *para* to the imino-group it would not be surprising if a small amount of the homologue were synthesised by condensation reactions in the course of the process. It was also shown that a mixture of 4-methylcarbazole and carbazole afford no 3-methylcarbazole under the conditions employed, although naturally it would never be feasible to eliminate the possibility of migration of groups at an earlier stage.

Up to this point it seemed safe to conclude that N(b) is attached to position 3 of a partly reduced carbazole nucleus in the strychnine molecule. We hoped to clinch the matter by introducing a methyl group in a different position, and for this purpose selected oxodihydro-*neo*strychnine (see the preceding paper) as the starting point. This base probably contains :N(b)·C·CO·, and reaction with methylmagnesium iodide should result in attachment of methyl to the β-carbon with respect to N(b). Hence the result of degradation was expected to be 4-methylcarbazole (or 2-methylcarbazole). The outcome was surprising since the carbazole fraction of the degradation product contained about 10% of 3-methylcarbazole as found by infra-red absorption analysis. Unidentified substances were also present. Now whatever the constitution of strychnine may be, it is anomalous that these two degradations should have given the same result. It is inescapable that migration must have occurred in one of the cases unless, indeed, the methyl group of 3-methylcarbazole does not arise from that introduced into the strychnine molecule. It will be seen that the clarity of an argument that could be developed is obscured by the necessity to exercise judgment in the interpretation of the results.

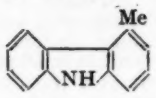
Synthesis of 4-Methylcarbazole.—According to Plancher and Carrasco [*Roy. Acad. Lincei*, 1904, (V), **13**, (i), 632, cited by Hollins, " Synthesis of Nitrogen Ring Compounds," p. 168] the

Fischer reaction applied to 3-methyl*cyclo*hexanone phenylhydrazone affords a mixture of 2- and 4-methyltetrahydrocarbazole; Borsche, Bothe, and Witte (*Annalen*, 1908, **359**, 61) found only the 2-methyl derivative. (Owing to a special numbering system this is described as the 4-methyl derivative, but it gives 2-methylcarbazole on dehydrogenation.) To effect an unambiguous synthesis it was preferable to start with a *m*-tolylhydrazine, and we blocked the 4-position by a chlorine atom.

4-Chloro-*m*-toluidine (Gattermann and Kaiser, *Ber.*, 1885, **18**, 1600) was converted in the usual manner into the *hydrazine* and then into 8-*chloro*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*



(I.)



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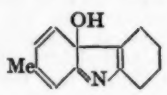

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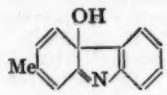

(IV.)

(I) by heating with dilute sulphuric acid; a by-product is discussed below. (I) was dehydrogenated by chloranil with formation of 1-*chloro*-4-*methylcarbazole* and converted into 4-*methylcarbazole* (II) by heating with palladised charcoal in a stream of hydrogen.

The by-product mentioned above contained a trace of chlorine and hence gave low results for carbon. It appears, however, to be $C_{13}H_{15}ON$. It was dehydrogenated by palladised charcoal to a substance $C_{13}H_{11}ON$ which gave sharp results on analysis. These curious compounds are devoid of phenolic character and do not form picrates. The constitutions (III) and (IV) are suggested provisionally. It is hoped that an opportunity to make a further examination of these substances will be found.

Added in Proof (*November 9th*, 1947).—We now know that oxodihydro*neo*strychnine is a derivative of *allo*strychnine and is an aldehyde. The methyl introduced by the Grignard reagent is remote from the carbazole nucleus. Therefore the formation of 3-methylcarbazole is probably due to rearrangement or synthesis in the course of the degradation process.

Experimental.

Degradation of Strychnineacetic Acid.—Pseudostrychnine was prepared by the elegant method of Leuchs (*Ber.*, 1940, **73**, 734) who states that strychnine (100 g.) yields crude pseudostrychnine (41—43 g.), neutral product (10—15 g.), and unchanged strychnine (30—33 g.). Our experience of several runs is that the respective average figures are 54, 20, and 4.

This crude pseudostrychnine (43 g.) was converted into strychnineacetic acid (Leuchs, *loc. cit.*) by condensation with malonic acid. The isolated perchlorate was powdered with animal charcoal and extracted with water in a Soxhlet apparatus (39 g.). On treatment with N-sodium bicarbonate solution (69 c.c.) and continuous extraction with chloroform, strychnineacetic acid (30 g.) was obtained. This was then heated in batches (6 g.) for 0·5 hour at 280—300°; a brown powder (25 g.) was obtained. Leuchs (*Ber.*, 1943, **76**, 1069) claims that methylstrychnine can be obtained in 17—25% yield by this method. This was powdered in 5 g. lots with soda-lime (30 g.) and heated in a metal-bath at 380—400° for 1 hour. The distillate, a brown tar, was extracted with benzene, washed with acid and alkali and steam-distilled. After about 10 l. had distilled, no further volatile substances came over. The distillate was extracted with benzene, concentrated, and passed through an alumina column. The first washings were found to be light yellow and fluorescent in ultra-violet light. These were concentrated and the resultant crystals were recrystallised from light petroleum (b. p. 60—80°). After sublimation in a high vacuum at 160°, a white solid (30 mg.) was obtained. It had a faint indolaceous odour, m. p. 203—207° after shrinking at 199° (Found: C, 86·0; H, 5·9; *C*-Me, 3·7%). On being kept in the air it became light brown. When this substance (3 mg.) was treated with picric acid (3·6 mg.) in benzene, a red-brown picrate, m. p. 156—162°, was obtained. The white solid dissolved in concentrated sulphuric acid to a very pale yellow solution which became ultramarine blue on the addition of a drop of concentrated nitric acid. When it was dissolved in alcohol and an acid solution of *p*-nitrobenzenediazonium chloride added, a bright yellow coloration developed. Infra-red measurements indicate that the mixture contains about 8—12% of 3-methylcarbazole along with carbazole. None of the other methylcarbazoles were detected but a small amount of some impurity was also found to be present.

The following experiments were made for comparative purposes.

Carbazole. When recrystallised from benzene the specimen employed had m. p. 238° (Found : *C*-Me, 0·85. Calc.: C, 86·2; H, 5·4; *C*-Me, 0·0%). The yellow solution in concentrated sulphuric acid became ultramarine blue on the addition of a drop of concentrated nitric acid. Its solution in alcohol became pale pink on the addition of an acidified solution of *p*-nitrobenzenediazonium chloride. The picrate (bright red) had m. p. 183—184°; mixed m. p. with the unknown picrate, 157—160°. The melting points of mixtures of carbazole and 3-methylcarbazole, and of carbazole and 4-methylcarbazole are shown below :

Carbazole and 3-methylcarbazole.

Carbazole, %	4	16	27	38	52	62	79	89	95
Softening pt.	200°	198°	198°	203°	210°	213°	220°	228°	234°
M. p.....	200—202°	199—201°	201—203°	205—207°	212—214°	214—217°	224—227°	231—233°	237—238°

Carbazole and 4-methylcarbazole.

Carbazole, %	4	13	24	36	53	62·5	75	87·5	94·5
Softening pt.	110°	110°	107°	117°	130°	175°	190°	224°	230°
M. p.....	112—117°	113—117°	115—150°	140—174°	168—196°	198—220°	214—224°	228—232°	235—236°

A mixture of the unknown with an equal quantity of a 3-methylcarbazole–carbazole mixture (60 : 40) softened at 198° and had m. p. 202—205°.

3-Methylcarbazole. The specimen had m. p. 202° (Found: *C*-Me, 6·0. Calc.: C, 86·2; H, 6·1; *C*-Me, 8·3%). It gave a colourless solution in concentrated sulphuric acid which turned emerald green upon the addition of a drop of concentrated nitric acid. Its alcoholic solution became faintly yellow upon the addition of *p*-nitrobenzenediazonium chloride. The dark red picrate had m. p. 178—179°; mixed m. p. with the unknown picrate, 155—158°; mixed m. ps. with carbazole picrate were 158—162° (33%, carbazole picrate), 160—164° (50%), 160—164° (66%).

A mixture of carbazole (20 mg.) and 3-methylcarbazole (20 mg.) could not be separated by chromatography under the conditions employed.

4-Methylcarbazole (Found: *C*-Me, 5·7%). The colourless solution in sulphuric acid became ultramarine blue on the addition of nitric acid. Its alcoholic solution gave a yellow-brown coloration with *p*-nitrobenzenediazonium chloride.

From these results it appears that the degradation product contains a compound, affording acetic acid in the Kuhn–Roth estimation of side-chain methyl, other than the 10% of 3-methylcarbazole indicated by the infra-red analysis. The faint indolaceous odour and the colour reactions suggest that this may be an indole derivative, but the possibility of the presence of higher homologous carbazoles cannot be dismissed.

The residue in the flask from the degradation reaction was found to contain a fluorescent acid substance. It gave the carbazole reaction with sulphuric–nitric acid but was obtained in such small quantity that further examination was precluded. When strychnine was distilled over soda-lime at 400°, carbazole, m. p. 229—232°, could be isolated in the manner described above. The specimen had the usual faint indolaceous odour and became light brown in colour on being kept for a few days. The infra-red spectrum showed strong carbazole bands at 845 cm.$^{-1}$ and 857 cm.$^{-1}$, a weak band at 810 cm.$^{-1}$ (3-methylcarbazole, $<1\%$), and a very weak band at 787 cm.$^{-1}$, which was not found with carbazole or any of the four *C*-methylcarbazoles. A mixture of carbazole (60 mg.) and 4-methylcarbazole (40 mg.) was heated with soda-lime (30 g.) for an hour at 380—400°. The distillate was collected by means of acetone and sublimed, m. p. 192—217°; carbazole–4-methylcarbazole (62·5 : 37·5), m. p. 198—220°. Infra-red examination showed the presence of carbazole and 4-methylcarbazole, but the absence of 3-methylcarbazole could not be categorically affirmed because 4-methycarbazole has a band at 812 cm.$^{-1}$ in the vicinity of that of 3-methylcarbazole at 808 cm.$^{-1}$. However in the graph obtained there was no appreciable broadening of the 812 band towards 808.

ββ-N(b)-Hydroxymethyldihydroneostrychnine.—A Grignard solution was prepared from magnesium (13 g.), methyl iodide (23·5 c.c.), and ether (300 c.c.); after the addition of anisole (200 c.c.), the ether was distilled (bath at 100°). A solution of oxodihydro*neo*strychnine (28·5 g. of the base, 1 MeOH) in anisole (350 c.c.) was added and the whole heated for 5 hours at 100°. After being poured on ice, the product was extracted by dilute hydrochloric acid and the solution basified with ammonia (dried as a light yellow solid, 27·5 g.). A portion was crystallised from alcohol (charcoal) and from benzene–light petroleum (b. p. 80—100°) and obtained as prismatic needles, which shrank at 130°, m. p. 160° (decomp.) (Found: C, 72·5; H, 7·2. $C_{23}H_{26}O_3N_2$ requires C, 72·1; H, 7·1%). This *base* (5 g., crude) was ground with soda-lime (25 g.) and distilled at 400°, and the product from five such batches was worked up in the manner already described. The carbazole fraction had m. p. 116—200°. The infra-red spectrum showed strong bands at 810 cm.$^{-1}$ (3-methylcarbazole, *ca.* 10%), the carbazole bands at 845 cm.$^{-1}$ and 857 cm.$^{-1}$, and a very weak band at 787 cm.$^{-1}$ (see above). The absence of 4-methylcarbazole is not established owing to the possible swamping of its relatively weak characteristic bands by stronger neighbouring absorption due to carbazole and 3-methylcarbazole. The low m. p. suggests the presence of 4-methylcarbazole or of some other unidentified constituent.

4-Chloro-m-tolylhydrazine.—A hot solution of 4-chloro-*m*-toluidine (5·8 g.) in dilute hydrochloric acid (67 c.c. containing 11 c.c. of concentrated acid) was added to concentrated hydrochloric acid (107 c.c.), cooled to 0°, and diazotised by addition of sodium nitrite (3·2 g.) dissolved in a little water. The diazo-solution was poured into an ice-cold solution of stannous chloride (21 g.) in concentrated hydrochloric acid (26 c.c.). After an hour at 0° the mixture was kept for 12 hours at the room temperature, the solid collected, washed with saturated brine, and triturated with a solution of sodium hydroxide (17 g.) in water (50 c.c.). The base was collected, washed with water, and dried (3·8 g. or 59%). The *substance* crystallised from water in needles, m. p. 61° (Found: C, 53·5; H, 5·6. $C_7H_9N_2Cl$ requires C, 53·7; H, 5·8%). A mixture of *cyclo*hexanone (2·4 g.), 4-chloro-*m*-tolylhydrazine (3·6 g.), and ethanol (10 c.c.) was refluxed for an hour and added to water. The product was isolated by means of ether (yield, 4·8 g.), and it crystallised from alcohol in plates, m. p. 58°.

The crude *cyclo*hexanone 4-chloro-*m*-tolylhydrazone (from 5·7 g. of chlorotolylhydrazine) was boiled with a mixture of concentrated sulphuric acid (10 c.c.) and water (90 c.c.) for 5 minutes; chloride ion was detected in the aqueous solution. The red oil was extracted with ether leaving a pink solid (0·35 g.) which crystallised from alcohol in dark red needles, m. p. 195—197° (decomp.), and contained nitrogen and chlorine (Found: C, 66·0; H, 4·9; N, 6·1%). The nature of this compound has not been discovered. The oil from the ethereal extract was distilled, b. p. 222—223°/20 mm. (5·7 g.), and treated with light petroleum (b. p. 40—60°). An insoluble white solid residue (0·7 g.) crystallised from aqueous alcohol (charcoal) in white needles, m. p. 199—201° (decomp.) [Found: C, 76·8; H, 7·4; N, 6·9; *M* (Rast in camphor), 220. $C_{13}H_{13}ON$ requires C, 77·6; H, 7·5; N, 7·0%; *M*, 201]. The low percentage of carbon found is due to a trace of chlorine the presence of which was shown by the Beilstein test. This *compound*

(A) will be further examined. The light petroleum solution was concentrated and afforded 5·0 g. of a pale yellow solid. Recrystallisation from aqueous ethanol gave colourless needles, m. p. 64·5° (Found : C, 70·4; H, 6·5. $C_{13}H_{14}NCl$ requires C, 71·0; H, 6·4%). When the specimens of this *8-chloro-5-methyl-1 : 2 : 3 : 4-tetrahydrocarbazole* (I) were examined after a lapse of months, in order to repeat the analysis, it was found that they had decomposed with formation of dark resins.

4-Methylcarbazole (II).—Chloromethyltetrahydrocarbazole (0·5 g.) and palladised charcoal (0·15 g.) were heated (bath at 280—300°) in a stream of hydrogen; evolution of hydrogen chloride ceased after 2 hours.

The mass was extracted with acetone and the methylcarbazole precipitated by addition of water (0·38 g.). The *compound* crystallised from aqueous ethanol as small white needles, m. p. 115—116° (Found : C, 85·8; H 6·2. $C_{13}H_{11}N$ requires C, 86·1; H, 6·1%). The *picrate*, m. p. 160·5°, separated from benzene in red needles (Found : C, 56·0; H, 3·6. $C_{19}H_{14}O_7N_4$ requires C, 55·6; H, 3·4%). Other properties of 4-methylcarbazole are mentioned above.

When the compound (A), $C_{13}H_{15}ON$, was similarly dehydrogenated, 0·33 g. gave 0·25 g. of solid material. This crystallised from aqueous ethanol as white needles, m. p. 262° (decomp.) [Found : C, 79·2; H, 5·8; N, 7·2; *M* (Rast in camphor), 195. $C_{13}H_{11}ON$ requires C, 79·2; H, 5·6; N, 7·1%; *M*, 197]. This *substance* is isomeric with a methylphenoxazine, but phenoxazine has m. p. 156° and 2-methylphenoxazine has m. p. 123—125°, so that it is unlikely to be 3-methylphenoxazine. The only alternative we can suggest is (IV) whence the tetrahydro-derivative (A) should be (III). The stability of these substances is noteworthy.

1-Chloro-4-methylcarbazole.—Chloromethyltetrahydrocarbazole (1·5 g.) was oxidised by chloranil in xylene according to the method of Barclay and Campbell (*J.*, 1945, 530). The resultant dark oil afforded a *picrate* (2·1 g.) which crystallised from benzene in dark red needles, m. p. 154·5° (Found : C, 51·7; H, 3·3. $C_{19}H_{13}O_7N_4Cl$ requires C, 51·3; H, 2·9%). The *chloromethylcarbazole* crystallised from aqueous ethanol in slender, white needles, m. p. 70° (Found : C, 71·6; H, 4·4. $C_{13}H_{10}NCl$ requires C, 72·4; H, 4·7%).

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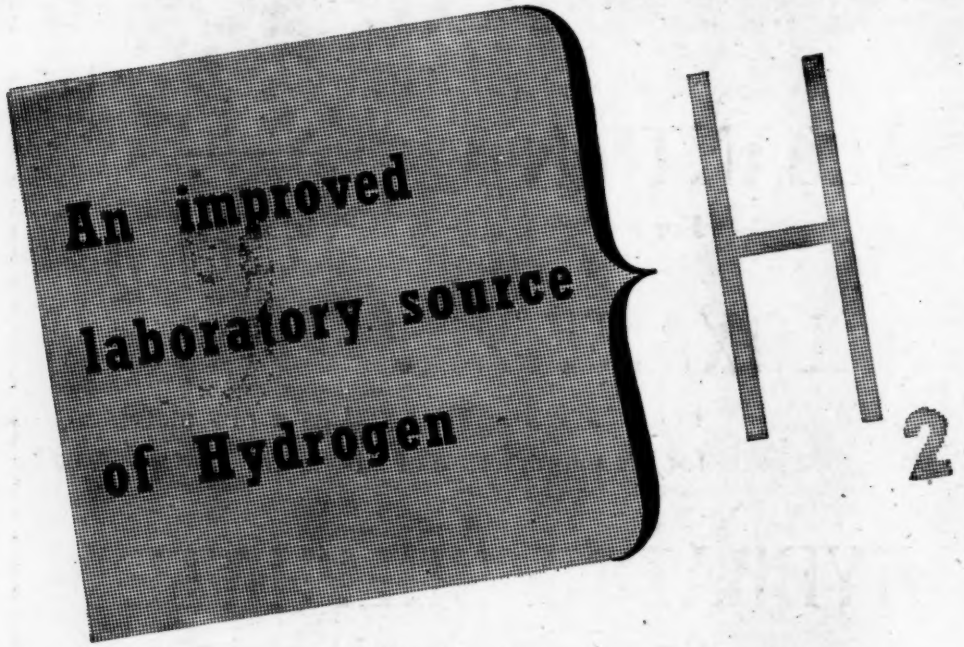

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